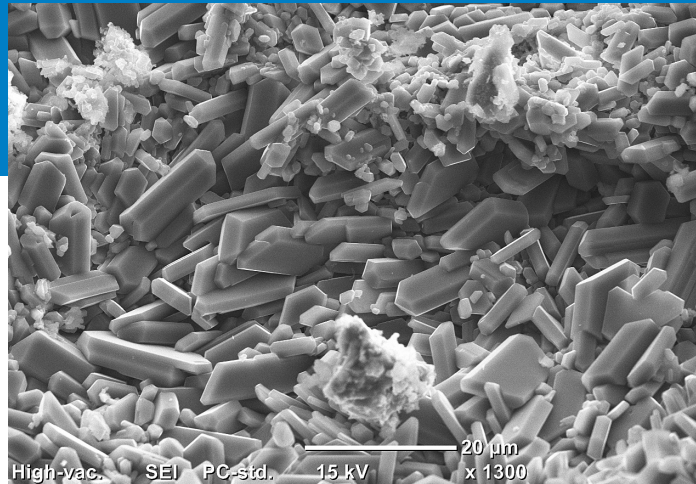


An ACI Technical Publication

SYMPOSIUM VOLUME



Sulfate Attack on Concrete: A Holistic Perspective

Editors:

Mohamed T. Bassuoni, R. Doug Hooton and
Thanos Drimalas

SP-317



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First printing, June 2017

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Printed in the United States of America

Editorial production: Aimee Kahaian

ISBN-13: 978-1-945487-67-5

Preface

The papers presented in this volume were included in a three-part session sponsored by ACI Committee 201, Durability of Concrete, about sulfate attack on concrete at the ACI Convention in Philadelphia, PA, on October 23-24, 2016. In line with the practice and requirements of the American Concrete Institute, peer review, followed by appropriate response and revision by authors, has been used.

Deterioration of concrete due to sulfate attack is a complex process characterized by multiple damage manifestations including volumetric expansion, cracking, spalling, softening, and in some cases mushiness. Sulfate attack can generally be classified as internal or external to the cementitious matrix, and the underlying damage modes can be chemical or physical. The scope of papers involves a multitude of theoretical and experimental aspects of different forms of sulfate attack. Readers are urged to critically evaluate the work presented herein, in the light of the large body of knowledge and scientific literature on this durability topic.

We dedicate this volume of papers to the memory of Prof. Robert L. Day, past chairman of Canadian Standards Association (CSA) Committee A23.1/A23.2 (Concrete Materials and Construction), for his invaluable contributions to the field of durability of concrete.

The editors sincerely thank all the presenters in this session and authors of the articles included in this SP, as well as the reviewers for their objective assessment of the papers. Their technical contributions provided a holistic perspective of sulfate attack on concrete.

Mohamed T. Bassuoni, Chairman and Editor
R. Doug Hooton, Co-chairman and Co-editor
Thanos Drimalas, Co-chairman and Co-editor

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Criteria for Concrete Mixtures Resistant to Chemical Sulfate Attack

Karthik H. Obla and Colin L. Lobo

SYNOPSIS:

This paper presents research on the sulfate resistance of concrete mixtures as it relates to ACI 318 Code requirements for sulfate resistance. The study evaluates the provisions of ACI 318 for various concrete mixtures containing sulfate resisting portland cements and supplementary cementitious materials with w/cm varying between 0.40 and 0.60. The sulfate resistance of concrete mixtures was evaluated using prolonged exposure in a concentrated sulfate solution in accordance with USBR Test 4908. The results on the concrete evaluation reveal that the ACI requirements are considerably conservative for most concrete mixtures that contain a sulfate resisting cementitious system with supplementary cementitious materials. Sulfate resisting portland cements did not perform as well in the associated exposure class defined in ACI 318. While a performance-based alternative to the requirement for a maximum w/cm was attempted, no clear criteria could be achieved. The paper proposes alternative criteria to those in ACI 318 for sulfate resistance based on the performance of concrete mixtures evaluated in this study.

KEYWORDS:

ACI 318, chemical sulfate attack, Code requirements, specifications, sulfate resistance

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INTRODUCTION

Exposure of concrete members to water-soluble sulfates from external sources can be a significant cause of deterioration. This type of durability problem is typically prevalent where higher sulfate concentrations are present in soil or water in contact with concrete. It can also be an issue in facilities that generate sulfate bearing solutions that will come in contact with concrete. There are three types of phenomenon observed when concrete members are exposed to an external source of sulfates¹ – chemical sulfate attack²; physical sulfate attack resulting from crystallization of some salts of sulfate^{3, 4, 5}; and thaumasite formation when concrete mixtures contain finely divided carbonates^{6, 7}.

This paper is limited to chemical sulfate attack, often referred to as *classical* sulfate attack. Chemical sulfate attack is governed by two factors^{1, 8, 9}:

1. Type and characteristics of cementitious materials – Increased quantity of tri-calcium aluminate phase, C_3A , in portland cement decreases its sulfate resistance. Aluminate phases in some supplementary cementitious materials (SCM), such as in some Class C fly ash¹⁰, or higher alumina content in slag cement¹¹, can contribute to sulfate attack.
2. Permeability of concrete – Water-soluble sulfates penetrate concrete by a combination of capillary sorption and diffusion. Concrete mixtures with a low w/cm and containing SCM reduce the rate of penetration of sulfates into the concrete.

The ACI 318 Building Code, ACI 318-14¹², limits its durability provisions to chemical sulfate resistance in the sulfate exposure category. It defines sulfate exposure classes based on the concentration of sulfate in soil or water concrete members will be exposed to. The requirements for concrete mixtures that will be exposed to these exposure classes are summarized in Table 1. ACI 318-14 also permits a cementitious materials combination that has been qualified when tested by ASTM C1012¹³ with expansion criteria listed in Table 1. Service records of acceptable performance of concrete mixtures containing SCM are also permitted in lieu of ASTM C1012 tests.

The objective of this research project was to evaluate the current requirements for sulfate resistance in ACI 318 and to evaluate whether a rapid index test that provides an indicator of the permeability of concrete could be proposed as an alternative to the maximum w/cm. The maximum w/cm limit is invoked as a prescriptive requirement to reduce the permeability of concrete that controls the rate of penetration of water-soluble sulfates from external sources into the concrete. Besides w/cm, however, the permeability of concrete is also impacted by the composition of the cementitious materials used in the mixture and this benefit from using SCMs is not accounted for in the current provisions.

The sulfate resistance of concrete was evaluated by a long-term immersion test used by the US Bureau of Reclamation (USBR) in their research work on sulfate resistance. A modified version of USBR 4908¹⁴ test was used

in this study. The level of sulfate resistance of concrete in USBR 4908 was related to the performance of cementitious materials in ASTM C1012 and other mixture characteristics. Based on these comparisons alternative requirements for chemical sulfate resistance are proposed.

MATERIALS AND MIXTURES

The following materials were used:

- ASTM C150¹³ Type I portland cement (PC-I) with $C_3A = 12\%$;
- ASTM C150 Type II portland cement (PC-II) with $C_3A = 8\%$;
- ASTM C150 Type V portland cement (PC V-1) with $C_3A = 3\%$,
- ASTM C150 Type V portland cement (PC V-2) with $C_3A = 5\%$,
- ASTM C618¹⁵ Class F fly ash (FA) – $CaO = 0.7\%$
- ASTM C989¹⁵ Grade 120 Slag Cement – $Al_2O_3 = 11.8\%$
- ASTM C778¹³ standard graded sand for C1012 tests
- ASTM C33¹⁵ natural sand, fineness modulus 2.88
- ASTM C33 No. 57 crushed stone coarse aggregate
- ASTM C494¹⁵ Type A polycarboxylate-based water reducing admixture and Type F polycarboxylate-based high range water reducing admixture

ASTM C1012 was conducted on mortar mixtures with selected combinations of cementitious materials as indicated in Table 2.

Twenty two non air-entrained concrete mixtures were made with ASTM C150 Types I, II and V portland cements, varying quantities of slag cement and Class F fly ash, and with w/cm varying between 0.40 and 0.60. The mixtures were evaluated in two separate series. Mixture parameters were selected for different levels of sulfate resistance and to attempt to characterize mixture performance within the four ACI 318 exposure classes for sulfate resistance. Mixture designations were provided to denote the type of mixture: “w/cm; SCM type; SCM quantity; and portland cement type”. Mixtures with only portland cement are denoted with “PC”. Mixture designations and parameters are provided in Table 3.

TEST PROCEDURES

Several cementitious material combinations were tested for sulfate resistance in accordance with ASTM C1012. Mortar bars were immersed in 5% sodium sulfate solution after achieving the minimum strength required by the test method. This method uses a fixed w/cm of 0.485 and its purpose is to evaluate the cementitious materials for sulfate resistance. Expansion criteria in ACI 318 extend to 18 months for the more severe exposure class. In this study, the duration of immersion in sulfate solution was extended to 36 months. Mixture parameters and test results for ASTM C1012 are provided in Table 2.

The concrete mixtures were mixed in a revolving drum laboratory mixer in accordance with ASTM C192¹⁵. A dosage of 3 oz/cwt. (195 mL/100 kg) of the Type A water-reducing admixture was used for all concrete mixtures. The dosage of the Type F high-range water-reducing admixture was varied to attain a target slump between 4 and 7 in. (100 and 175 mm).

Fresh concrete was tested for slump in accordance with ASTM C143¹⁵, temperature in accordance with ASTM C1064¹⁵, air content by the pressure method in accordance with ASTM C231¹⁵, and density in accordance with ASTM C138¹⁵. The gravimetric air content was also calculated in accordance with ASTM C138.

Compressive strength of test specimens from the concrete mixtures was tested in accordance with ASTM C39¹⁵. The strength reported is the average of two 4 × 8 in. (100 × 200 mm) cylindrical specimens at an age of 28 days.

From the concrete mixtures, samples were prepared to measure the transport properties of concrete mixtures. Only results of the rapid chloride permeability tests, ASTM C1202¹⁵, are reported here. For these tests 4 × 8 in. (100 × 200 mm) cylindrical specimens were cast. Specimens were subjected to three curing procedures and durations:

- Accelerated curing, in accordance with ASTM C1202, and tested at an age of 28 days;
- Moist cured and tested at an age of 56 days; and

- Moist cured and tested at an age of 1 year.
- The top 2 in. (50 mm) from the finished surface of the cylinder was tested. Results reported are the average from two specimens.

The sulfate resistance of concrete mixtures was evaluated using USBR 4908. Method B involves immersion of test specimens in 10% sodium sulfate solution. Method B was used with some variations on the specimen type and pre-conditioning prior to immersion. Specimens subjected to immersion were expected to deteriorate primarily due to chemical sulfate attack due to the inwards migration of the sulfate ions from the specimen surface. In this study $3 \times 3 \times 11\frac{1}{4}$ in. ($75 \times 75 \times 280$ mm) concrete prism specimens were used. The specimens were moist cured for 28 days followed by air drying for 28 days before immersion in the solution. The specimens were immersed in the sulfate solution for 48 months or until it had experienced significant expansion or deterioration. The USBR has used a failure criterion as expansion that exceeds 0.5% and this was found to correlate with about 40% loss in dynamic modulus of elasticity¹⁶. The USBR test uses 3×6 in. (75×150 mm) cylinders as opposed to the prismatic specimens used in this study. Periodic measurements of length change, mass change, and visual rating of specimen condition were performed. For each condition, results reported are the average of two specimens.

At the termination of the immersion period of the concrete specimens in the sulfate solution, visual rating of specimen condition was observed by three laboratory personnel with the following guidelines:

- 0 – considerable cracking and spalling of concrete at corners and edges
- 1 – Moderate cracking; some loss of concrete due to spalling; and damage at edges
- 2 – Moderate cracking and edge damage but no loss of concrete due to spalling
- 3 – Minor cracking and no loss of concrete.

The impact of sulfate attack on the strength for some of the concrete mixtures was also evaluated. After the immersion period two 3×3 in. (75×75 mm) cubes were obtained from a single prism for each mixture. The cubes were tested in compression and the measured average strengths were modified by a correction factor of 0.75 to estimate the cylinder strength from that measured on the cubes. Additionally, strength of cylinders moist cured for 43 months was also measured.

Additional details of concrete mixture proportions, fresh concrete and other transport indicator tests are reported elsewhere¹⁷.

RESULTS AND DISCUSSION

Results of ASTM C1012 Tests

The cementitious material combinations and the expansion results for the 10 mortar mixtures tested in accordance with ASTM C1012 tests reported in Table 2 and illustrated in Figure 1. The mixture parameters were selected to reflect a range of sulfate resistance of the cementitious materials used. These results are consistent with expectations for sulfate resistance. ACI 318 criteria for C1012 expansion extend to up to 18 months for the most severe exposure class (S3). These tests were continued for 36 months to observe if any later age expansion occurred. As expected, expansion decreased when the SCM quantity increased and/or the C_3A content of the portland cement decreased. Based on the expansion results, the ACI 318 Exposure Class applicable to these cementitious combinations is indicated in Table 2. The expansion associated with the ACI 318 expansion criteria is highlighted in Table 2 and denoted in Figure 1.

Expansion of the mortars with portland cements conform to the applicable ACI 318 exposure classes for cement type. All mixtures with fly ash and slag cement had superior sulfate resistance within the 18-month period and qualify to be used for the most severe Exposure Class S3. One exception is the mixture with 15% fly ash with Type I portland cement, which barely passed the expansion criteria (0.10% at 12 months) for Exposure Class S2 with an expansion of 0.09% at 12 months. The rate of expansion increased after this period. With this exception, all other mixtures containing SCMs had equal to or better sulfate resistance than mixtures with the Type V portland cements used in this study.

Increasing later age expansion is observed for the three sulfate resisting portland cement mixtures. An increasing expansion trends at later ages is observed for mixtures with Type I cement and 15% fly ash and to a lesser extent for the mixtures with Type I cement with 25% slag cement and that with Type II cement with 20% fly ash.

ACI 318 does not permit a Type I portland cement with 12% C_3A to be used for sulfate resistance, unless a cementitious material combination complies with the C1012 expansion criteria. It does permit the use of portland cement with up to 10% C_3A for concrete in seawater exposure (Exposure Class S1) provided the w/cm of the concrete does not exceed 0.40. This recognizes that C_3A improves binding of chlorides from seawater that can beneficially impact corrosion of reinforcing steel.

Concrete Mixtures

The parameters of the concrete mixtures tested in two series and selected test results are provided in Table 3. The test results reported are the 28-day compressive strength, ASTM C1202 results for specimens moist cured for 56 days, and the expansion and visual deterioration ratings for specimens tested by USBR 4908 at the termination of the immersion period or when immersion was terminated due to specimen failure. Immersion of concrete specimens in the 10% sodium sulfate solution was terminated at 48 months.

Expansion—For specimens tested by USBR 4908 all the portland cement mixtures without SCMs had high expansions. Considering an expansion level of 0.05% as failure, the Type I portland cement mixture exceeded this limit at nine months; Type II at 15 months; Type V-1 (3% C_3A) at 30 months; and Type V-II (5% C_3A) at 40 months. These high expansions were associated with considerable deterioration as indicated by the visual rating in Table 3. The rate of deterioration was related to the C_3A content of the portland cement used in these mixtures.

In Series 1 the concrete mixtures contained lower quantities of SCM (15% fly ash and 25% slag cement) with Type I portland cement. The expansion and visual deterioration increased as the w/cm of the concrete mixtures increased. The expansion for the mixtures containing SCM in Series 1 at a w/cm of 0.60 exceeded the 0.05% expansion level at around 16 months. The mixtures containing SCM at a w/cm of 0.40 performed extremely well for the duration of the test.

In Series 2, with higher quantities of SCMs and sulfate resisting portland cement, the higher expansion and level of deterioration is evident with increase in w/cm but differences are not that significant, with one exception. Mixture 0.6SL35-II showed the highest expansion and level of deterioration. This mixture exceeded the 0.05% expansion limit at about 42 months and there was modest visual deterioration of the specimens. The six mixtures containing Type V cement (V-1) with SCMs at all w/cm tested showed the lowest level of visual deterioration.

These data indicate that the mixtures with SCMs and Type I portland cement in Series 1 were less sulfate resistant than those in Series 2 with the Type II and Type V portland cements, as expected. The exceptions are for the mixtures in Series 1 with w/cm at 0.40.

Change in Mass—The change in mass of concrete specimens immersed in the sulfate solution is not reported here. The specimens were air-dried for 28 days prior to immersion and an increase in mass was observed for all mixtures due to absorption of the sulfate solution. Mixtures with a higher w/cm had a higher gain in mass. When deterioration progressed to the point of significant cracking, the rate of mass gain increased and subsequent spalling resulted in a loss in mass. Mass loss was primarily due to the corners of the prisms breaking off. Qualitatively, the specimen deterioration and increase or loss of mass generally corresponded to when the specimens exceeded the expansion limit of 0.05%. One exception was the 0.5PC-II mixture which had high expansion without any spalling and an associated decrease in mass.

Exposure Classification—In Table 3, Exposure Classes are assigned to the different concrete mixtures. In column titled “C1012”, the Exposure Class for the cementitious materials are listed as indicated in Table 2. The Exposure Class in the column titled “318” is based on the requirements in ACI 318. These are based on the C1012 expansion and the w/cm of the concrete mixtures. Sulfate resistance of the concrete mixtures evaluated in this study are assigned Exposure Classes in column titled “4908” based on their performance in the prolonged immersion as tested by USBR 4908. The assigned Exposure Class is based on the expansion level and the visual condition of the specimens represented by the numerical visual rating. Concrete mixtures tested by USBR 4908 that were categorized in Exposure class S0 exceeded the expansion level of 0.05% in 18 months; while mixtures categorized in Exposure Class S1 exceeded this expansion after 44 months. Concrete mixtures categorized as Exposure Class S2 and S3 categories had expansions less than 0.04% at 48 months. This assignment of Exposure Class for the concrete mixtures permits a comparison of the requirements for concrete mixtures in ACI 318 and the sulfate resistance of

concrete mixtures evaluated by USBR 4908. The mixtures where the exposure classification differs between ACI requirements and the performance of concrete mixtures in USBR 4908 are highlighted in the last two columns of Table 3.

In three cases the performance of the concrete mixtures in USBR 4908 was inferior to that expected by the ACI 318 requirements – the Exposure Class assigned from the USBR 4908 results suggest that these mixtures should be used in a less severe sulfate Exposure Class than what would be assigned in accordance with ACI 318. These were the portland cement mixtures (Types II, V-1, and V-2) without SCM.

In nine cases the performance of the concrete mixtures in USBR 4908 was superior to that expected by the ACI 318 requirements – the Exposure Class assigned from the USBR 4908 results suggest that these mixtures can be used at a more severe sulfate Exposure Class than what would be assigned in accordance with ACI 318. Eight of these nine mixtures contained supplementary cementitious materials and sulfate resistant cements (Type II and V). Of these, 4 cases are mixtures with a w/cm at 0.60 that likely will not be an acceptable requirement in ACI 318. However, the data illustrate that sulfate resistance is improved by the use of SCMs due to the increased sulfate resistance of cementitious material system (C1012 expansion) and an associated reduction of the permeability of concrete. The impact on the permeability of concrete can be surmised from the ASTM C1202 results in Table 3. In this regard, w/cm as a controlling requirement for sulfate resistance in ACI 318 may be lacking. These data suggest that a higher w/cm may be permitted with cementitious material system that is demonstrated to be more sulfate resistant and improves the permeability of concrete. In Series 2, the mixtures with a w/cm of 0.50 would comply with ACI 318 exposure class S1 but performed well enough to be used in exposure class S2 or even in S3 in one case. Mixture 0.40FA15-1 showed moderate sulfate resistance (S2) with the cementitious materials in ASTM C1012. This is a combination of the higher C₃A in the portland cement (12%) and the lower quantity of fly ash. However with a w/cm of 0.40, this mixture performed very well in the USBR 4908 test and could qualify to be used for Exposure Class S3.

It is noted that at this time ACI 318 provisions for sulfate resistance do not require concrete mixtures to comply with a maximum w/cm of 0.40. In this study, all concrete mixtures with a w/cm of 0.40 contained SCMs and performed very well to qualify to be used in Exposure Class S3 even when used with lower quantity of slag cement or fly ash and with the Type I portland cement (12% C₃A). There is a proposal in ACI 318, which would make it consistent with Canadian Standard CSA A23.1¹⁸, to permit Type V portland cement and mixtures that meet the C1012 expansion criteria for Exposure Class S2 to be used for Exposure Class S3 with a maximum w/cm of 0.40. This study did not include a Type V portland cement concrete mixture without SCMs at a w/cm of 0.40. However, since both 0.45 w/cm Type V mixtures without SCMs performed only to a sulfate exposure level of S1 in the USBR 4908 test it is unlikely that a 0.40 w/cm Type V mixture without SCM would have performed to a sulfate exposure level of S3. But results of this study do support this revision for mixtures that contain SCMs.

Permeability—One of the goals of this research was to evaluate whether a rapid test that provides an indicator of the permeability of concrete could be used as an alternative to w/cm. The results of 56-day moist cured specimens tested by ASTM C1202 are reported in Table 3. This may be considered a limiting test age for mixture qualification. It also reflects the age of the specimens when they were immersed in the sulfate solution for USBR 4908 tests. No clear relationship could be established between the sulfate resistance of concrete mixtures in USBR 4908 and an indicator of permeability for ASTM C1202 results obtained at 56 days. For this reason, no performance-based test criterion is proposed as an alternative to the max w/cm.

Additional ASTM C1202 tests were performed on specimens that were subjected to the accelerated curing as defined in ASTM C1202 and specimens moist cured for 1 year. These results are illustrated in Figure 2. For the portland cement mixtures the change in the charge passed is not significant between 56 days and 1 year. The average reduction of the charge passed is about 15%. For the mixtures with slag cement the reduction in the charge passed between the same ages is about 35%. However, for the mixtures with fly ash, there is a considerable improvement in this permeability indicator – the reduction in charge passed is about 75% between 56 days and 1 year. In this regard fly ash mixtures may not demonstrate low permeability characteristics at early ages but this considerably improves with age and continued curing. In this evaluation, accelerated curing did not have as much of an impact on the C1202 result compared to a longer moist curing period. From a practical standpoint, it is likely that concrete will be subjected to sulfate exposure at the time of construction – such as a footing or foundation in sulfate soils. But the section size and water-soluble sulfate concentration is not likely to cause deterioration to the level observed in the

USBR test and the sulfate resistance of these concrete members will improve with age. In some cases, such as in environmental engineering structures, the exposure to sulfates may be at a later age, when the sulfate resistance of mixtures containing SCMs can be expected to be at a higher level.

Compressive Strength—A comparison of compressive strength of cylinders moist cured for 28 days and 43 months, and cubes extracted from USBR 4908 test prisms after 48 months of exposure are illustrated in Figure 3 for selected mixtures. The strength of USBR 4908 specimens for the 0.5PC-II, 0.45PC-V1 and 0.5SL25-I mixtures were between 12% and 30% lower than their 28 day strengths. The 0.45PC-V2 mixture had about the same strength at both ages. The strength of the remaining 11 mixtures immersed in sulfate solution for 48 m were on average 40% higher than the 28-day strength. When the strength of USBR 4908 specimens is compared to the strength of cylinders moist cured for 43 months, these are about the same or slightly higher except for the two 0.45PC-V mixtures – these two mixtures had about 23% lower strength. The reduction in strength is consistent with the excessive deterioration observed for these mixtures. For the mixtures with a high sulfate resistance no loss in strength is observed.

PROPOSED CRITERIA

Chemical sulfate attack requires ingress of sulfate ions into the concrete and a cementitious system that is vulnerable to chemical sulfate attack. The results in this study illustrate that using a maximum w/cm as a primary criterion discounts the benefits of using SCMs on the permeability characteristics of concrete. A concrete mixture with lower permeability and lower chemical resistance may have similar sulfate resistance as a concrete mixture with a higher permeability and higher chemical resistance. This has been observed by other researchers¹⁹. It further suggests that with a more sulfate resistant cementitious material combination with SCMs, a higher w/cm can be used and provide the necessary sulfate resistance for different Exposure Classes. Concrete mixtures at a higher w/cm and lower strength are typically used for footings and foundations of structures. Permitting concrete mixtures that are sulfate resistant with a higher w/cm affords a more economical mixture that will be easier to place for these applications. This change is proposed for concrete that will be assigned to Exposure Classes S1 and S2. To remain conservative, however, this recommendation is not extended to concrete members that will be assigned to Exposure Class S3. This is supported by the performance of concrete mixtures with w/cm of 0.50 in Series 2.

For Exposure Class S3, C1012 testing for 18 months is a considerably long period. Blended cements complying with ASTM C595 and C1157 are tested for a period of 12 months to achieve the HS designation. To shorten the testing period for evaluating cementitious materials, it is proposed that mixtures meeting the C1012 criteria for Exposure Class S2 (0.1% at 12 months) can be used for concrete mixtures assigned to Exposure Class S3 if the maximum w/cm is 0.40. The mixture should contain SCMs that improve the sulfate resistance. It is further recommended, based on this study, that mixtures with Type V portland cement without SCMs at a maximum w/cm of 0.40 not be permitted for Exposure Class S3.

Based on the results of this study, these criteria for sulfate resistance are proposed. These recommendations are summarized in Table 4.

Exposure Class S1

- Type II portland cement and max w/cm of 0.50 (current ACI 318)
- Blended cement with MS designation and max w/cm of 0.50 (current ACI 318)
- Cementitious materials with ASTM C1012 expansion <0.10% @ 6 m (S1) and max w/cm of 0.50 (current ACI 318)
- Cementitious materials with ASTM C1012 expansion <0.10% @ 12 m (or <0.05% @ 6 m) (S2) and max w/cm of 0.55. Cementitious materials permitted should be SCM with Type II or Type V portland cements; or blended cements with HS designation without additional SCM (alternative)

Note that in this study, the Type II portland cement mixture at a 0.50 w/cm did not perform well in the USBR 4908 test to be used in Exposure Class S1. However, in the field, the rate of deterioration at a considerably lower concentration of water soluble sulfates will likely reduce the rate of deterioration to provide acceptable service life. With successful past field service records, a Type II portland cement without SCMs could be used for Exposure Class S1. The use of SCMs that improve the sulfate resistance of the cementitious materials is strongly recommended.

Exposure Class S2

- Type V portland cement and max w/cm of 0.45 (current ACI 318)
- Blended cement with HS designation and max w/cm of 0.45 (current ACI 318)
- Cementitious materials with ASTM C1012 expansion $<0.10\%$ @ 12 m (or $<0.05\%$ @ 6 m) (S2) and max w/cm of 0.45 (current ACI 318)
- Cementitious materials with ASTM C1012 expansion $<0.05\%$ @ 12 m and max w/cm of 0.50. Cementitious materials permitted should include SCMs with Type II or Type V portland cements; or blended cement with HS designation with additional SCM (alternative)

It is also noted in this study that the Type V portland cement mixtures at a 0.45 w/cm did not perform well in the USBR 4908 test to be used in Exposure Class S2. With successful past field service records, a Type V portland cement without SCMs could be used for Exposure Class S2. The use of SCMs that improve the sulfate resistance of the cementitious materials is strongly recommended.

Exposure Class S3

- Type V + SCM and max w/cm of 0.45 (current ACI 318)
- Blended cement with HS designation + SCM and max w/cm of 0.45 (current ACI 318)
- Cementitious material with ASTM C1012 expansion <0.1 @ 18 m (S3) and max w/c 0.45; (current ACI 318)
- Cementitious material with ASTM C1012 expansion <0.1 @ 12 m (S2) and max w/c 0.40; (alternative)

An exception to the last provision that the concrete mixture should contain SCMs that improve the sulfate resistance of the system. Based on the results of this study, it is recommended that a Type V portland cement without SCMs should not be used. ACI 318 does not specifically permit the use of Type I portland cement for sulfate resistance. It can be used if a cementitious mixture qualifies to the ASTM C1012 expansion criteria. In this study, concrete mixtures with Type I portland cement with SCMs and with a w/cm of 0.40 performed well in USBR 4908. The cementitious mixtures complied with the C1012 expansion criteria for Exposure Class S2. The use of cementitious materials with Type I cement is thereby not restricted in these alternative criteria for Exposure Class S3.

In line with ACI 318, the following minimum specified strengths apply to the max w/cm: 0.40 / 5000 psi (35 MPa); 0.45 / 4500 psi (31 MPa); 0.50 / 4000 psi (28 MPa); and 0.55 / 3500 psi (24 MPa).

The alternative criteria for Exposure Classes S1, S2 and S3 are based on the performance of concrete specimens subjected to long term exposure in concentrated sulfate solution (USBR 4908) in this study. The proposed alternative criteria establishes more consistent assignment of Exposure Classes to concrete mixtures based on the performance in USBR 4908. Even with the proposed alternative criteria, concrete mixtures performed at a higher level sulfate of resistance in USBR 4908 test in five conditions and all these mixtures contained SCMs. Of these, four mixtures with Type II or V portland cement and SCMs were at a w/cm of 0.60 and the performance in USBR 4908 suggest that these could be assigned to Exposure Classes S1 or S2. This suggests some conservatism in the proposed alternative criteria. In three conditions, the concrete mixtures performed at a reduced level relative to that expected by the ACI 318 criteria. In these conditions, concrete mixtures were composed of sulfate resisting portland cement (Type II and V) without SCMs. It is however suggested that if past field service records indicate successful performance, these options could be permitted.

ASTM C1202

No definitive recommendations can be made to replace the maximum w/cm with a specified charge passed requirement determined in accordance with ASTM C1202. Based on Figure 2, even if a conservative specified value of 1000 coulombs was used as a performance-based alternative to w/cm for exposure class S3, it would permit some of the mixtures with slag cement with a w/cm of 0.50 or higher. These mixtures did not perform well enough for exposure class S3 in the USBR 4908 test.

CONCLUSIONS

1. Expansion results on the evaluation of cementitious materials by ASTM C1012 for sulfate resistance was consistent with expectations and ACI 318 provisions.
2. Concrete mixtures evaluated for sulfate resistance with extended exposure in a 10% sodium sulfate solution in USBR 4908 suggest that ACI 318 provisions are conservative for mixtures containing SCMs with good sulfate resistance as determined by ASTM C1012. The mixtures with portland cement and no SCMs did not perform as well as expected by the ACI 318 provisions.
3. The use of w/cm as the primary provision for concrete mixtures in ACI 318 for sulfate resistance does not evaluate the benefits provided by SCMs in reducing the permeability of concrete. This study suggests that for cementitious material combinations with higher sulfate resistance, as determined by ASTM C1012, it might be appropriate to permit a higher w/cm for Exposure Classes S1 and S2. This will permit more economical concrete mixtures with improved ease of placement for foundations and lower load bearing members submerged in sulfate-bearing soil or water.
4. Concrete mixtures at a w/cm of 0.40 with SCMs indicated very high sulfate resistance with prolonged exposure in the USBR 4908 test. It is proposed that mixtures that contain SCMs and comply with the ASTM C1012 expansion criteria for Exposure Class S2 can be used for exposure class S3 with a w/cm of 0.40.
5. This study could not establish clear criteria to replace the w/cm requirement with an alternative permeability indicator test, such as ASTM C1202.

Acknowledgements

The authors would like to extend their sincere thanks to Mr. Soliman Ben-Barka and Mr. Stuart Sherman who performed the testing at the NRMCA Research Laboratory with assistance from Dr. Haejin Kim and Mr. Rongjin Hong. Funding for the study was provided by the Pooled Fund Study, and the RMC Research & Education Foundation.

References

1. Kosmatka, S.H. and Wilson, M.L., 2011, "Design and Control of Concrete Mixtures," Fifteenth Edition, Engineering Bulletin 001.15, Portland Cement Association, Skokie, IL, pp 444.
2. Mehta, P.K., 1986, "Concrete: Structure, Properties and Materials," Prentice Hall, Englewood Cliffs, NJ.
3. Stark, D., 2002, "Performance of Concrete in sulfate Environments," PCA RD129, Portland Cement Association, Skokie, IL, pp 28.
4. Haynes, H., O'Neill, R., Neff, M., and Mehta, P.K., 1996, "Concrete Deterioration from Physical Attack by Salts," Concrete International, V. 18, No. 1, pp. 63-68.
5. Haynes, H., and Bassouni, M. T., 2011, "Physical Salt Attack on Concrete," Concrete International, V. 33, No. 11, pp. 38-42.
6. Hobbs, D.W., 2002, "Thaumasite Sulfate Attack in Field and Laboratory Concretes: Implications For Specifications", in Proceedings of the first international conference on Thaumasite in Cementitious Materials, AP 147, Building Research Establishment, Garston, UK, 10 pp.
7. Irassar, E. F., 2009, "Sulfate attack on cementitious materials containing limestone filler — A review", Cement and Concrete Research, 39, pp. 241-254.
8. American Concrete Institute, 2008, ACI 201.2R-08, "Guide to Durable Concrete", Farmington Hills, MI, pp 49.
9. Neville, A., 2004, "The Confused World of Sulfate Attack on Concrete," Cement and Concrete Research, V. 34, No. 8, pp. 1275-1296.
10. Thomas, M. D. A., Shehata, M. and Shashiprakash, S. G., 1999, "The Use of Fly Ash in Concrete: Classification by Composition," Cement, Concrete and Aggregates, V. 12, No. 2, pp. 105-110.

11. Ogawa, S., Nozaki, T., Yamada, K., Hirao, H. and Hooton, R. D., 2012, "Improvement on Sulfate Resistance of Blended Cement with High Alumina Slag," *Cement and Concrete Research*, V. 42, No. 2, pp. 244-251.
12. American Concrete Institute, 2014, ACI 318-14, "Building Code Requirements for Structural Concrete", ACI 318R-14, "Commentary on Building Code Requirements for Structural Concrete", Farmington Hills, MI, 520 pp.
13. ASTM International, 2015, Annual Book of ASTM Standards, V 4.01, Cement: Lime; Gypsum, West Conshohocken, PA.
14. US Bureau of Reclamation, 1992, "USBR 4908 - Procedure for Length Change of Hardened Concrete Exposed to Alkali Sulfates," Part 2, 9th ed., Denver, CO.
15. ASTM International, 2015, Annual Book of ASTM Standards, V 4.02, Concrete and Aggregates, ASTM C150, C595, C778, C1012, C1157, West Conshohocken, PA.
16. Kalousek, G. L., Porter, L. C., and Harboe, E. M., 1976, "Past, Present, and Potential Developments of Sulfate-Resisting Concretes," *Journal of Testing and Evaluation*, ASTM International, Vol. 4, No. 5, pp. 346-354.
17. Obla, K.H., Lobo, C.L. and Kim, H., 2015, "An Evaluation of Performance-Based Alternatives to the Durability Provisions of the ACI 318 Building Code," Report submitted to the RMC Research and Education Foundation, January 2015, 123 pp., http://www.rmc-foundation.org/Concrete_Apps_Track.htm, Accessed Feb 1, 2016.
18. Canadian Standards Association, 2014, "A23.1-14/A23.2-14 - Concrete materials and methods of concrete construction/Test methods and standard practices for concrete" CSA Group, Mississauga, Ontario, Canada, 690 pp.
19. Khatri, R.P., Sirivivatnanon, V., and Yang, J. L., 1997, "Role of Permeability in Sulphate Attack," *Cement and Concrete Research*, V. 27, No. 8, pp. 1179-1189.

Table 1 - ACI 318-14 Requirements for Concrete Exposed to Sulfates

Exposure Class	Max. w/cm	Minimum f'_c , psi (MPa)	Cementitious Materials - Types			ASTM C1012 expansion
			ASTM C150	ASTM C595	ASTM C1157	
S0	N/A	2500 (17)	N/A	N/A	N/A	
S1	0.50	4000 (28)	II	Types IP, IS, or IT with (MS) designation	MS	0.10% at 6 m
S2	0.45	4500 (31)	V	Types IP, IS, or IT with (HS) designation	HS	0.05% at 6 m or 0.10% at 12 m
S3	0.45	4500 (31)	V plus pozzolan or slag cement	Types IP, IS, or IT with (HS) designation plus pozzolan or slag cement	HS plus pozzolan or slag cement	0.10% at 18 m

*Sulfate concentration in soil or water associated with exposure classes is in ACI 318-14

Table 2 - ASTM C1012 Mortar Mixture Proportions and Test Results

Mix ID	I	II	V1	V2	I-25SL	II-35SL	V1-50SL	I-15FA	II-20FA	V1-30FA
Cement Type	I	II	V-1	V-2	I	II	V-1	I	II	V-1
PC C ₃ A, %	12	8	3	5	12	8	3	12	8	3
Slag cement, %					25	35	50			
Fly ash, %								15	20	30
ASTM C1012 Expansion, %										
6 months	0.45	0.06	0.02	0.03	0.03	0.04	0.02	0.03	0.04	0.02
12 months	NA	0.16	0.05	0.04	0.04	0.04	0.02	0.09	0.04	0.02
18 months	NA	0.51	0.20	0.16	0.05	0.05	0.03	0.34	0.06	0.03
27 months	NA	1.07	0.38	0.33	0.08	0.05	0.03	0.61	0.12	0.04
36 months	NA	1.56	0.49	0.44	0.20	0.07	0.06	0.93	0.24	0.05
ACI 318 Exposure Class	S0	S1	S2	S2	S3	S3	S3	S2	S3	S3

Table 3 - Concrete Mixtures, Results, and Exposure Classes

Mix ID	PC	SCM, %		w/cm	Strength, psi ^a	C1202, coulombs ^b	USBR 4908		Exposure Class		
		SL	FA				Length Change, %	Visual Rating	C1012 (Exp, %) ^c	318	4908
Series 1											
0.5PC-I	I			0.50	5,690	2947	F (12) ^d	0	S0	S0	S0
0.5PC-II	II			0.50	6,440	3610	1.3	0	S1 (0.06)	S1	S0
0.4FA15-I	I		15	0.40	8,400	913	0.049	3	S2 (0.09)	S2	S3
0.5FA15-I				0.50	5,980	1593	0.071	1		S1	S1
0.6FA15-I				0.60	4,630	2627	F (33)	0		S0	S0
0.4SL25-I		25		0.40	9,540	704	0.034	3	S3 (0.05)	S3	S3
0.5SL25-I				0.50	7,700	1161	0.044	1		S1	S1
0.6SL25-I				0.60	5,710	1947	F (19)	0		S0	S0
Series 2											
0.45PC-V1	V-1			0.45	8,800	2861	0.138	1	S2 (0.05)	S2	S1
0.45PC-V2	V-2			0.45	7,720	3184	0.069	1	S2 (0.04)	S2	S1
0.4FA20-II	II		20	0.40	7,490	1848	0.036	3	S3 (0.06)	S3	S3
0.5FA20-II				0.50	5,310	2662	0.034	2		S1	S2
0.6FA20-II				0.60	3,990	3856	0.039	2		S0	S2
0.4SL35-II		35		0.40	10,020	705	0.034	3	S3 (0.05)	S3	S3
0.5SL35-II				0.50	6,740	943	0.035	2		S1	S2
0.6SL35-II				0.60	5,730	1790	0.054	1		S0	S1
0.4FA30-V1	V-1		30	0.40	7,610	1543	0.037	3	S3 (0.03)	S3	S3
0.5FA30-V1				0.50	4,870	3731	0.036	3		S1	S3
0.6FA30-V1				0.60	3,590	4772	0.036	2		S0	S2
0.4SL50-V1		50		0.40	7,500	593	0.031	3	S3 (0.03)	S3	S3
0.5SL50-V1				0.50	7,500	887	0.030	2		S1	S2
0.6SL50-V1				0.60	6,200	1077	0.035	2		S0	S2

^a Specimens moist cured for 28 days; 1 MPa = 145 psi^b Specimens moist cured for 56 days^c Expansion reported at the limiting test period – 6 m for S1; 12 m for S2; 18 m for S3^d Specimens failed (month terminated)

Table 4 – Summary of Current and Proposed Criteria for Sulfate Resistance

Exposure Class	Min f'_c , psi (MPa)	Max w/cm	Cement Type ^a	ASTM C1012 criteria	ACI 318 criteria
S0	2500 (17)	NA	NA	NA	Current
S1	4000 (28)	0.50	II or MS	0.10% at 6 m	Current ^b
	3500 (21)	0.55	(II or V) + SCM; or HS	0.10% at 12 m	Proposed ^c
S2	4500 (31)	0.45	V or HS	0.10% at 12 m	Current ^b
	4000 (28)	0.50	(II, V or HS) + SCM	0.05% at 12 m	Proposed ^c
S3	4500 (31)	0.45	V or HS + SCM	0.10% at 18 m	Current ^b
	5000 (35)	0.40	(I, II, V or HS) + SCM	0.10% at 12 m	Proposed ^c

^a ASTM C150 Type I, II or V; ASTM C595 Types IP, IS or IT with MS or HS designation; ASTM C1157 Type MS or HS

^b Cement Type and ASTM C1012 are alternate criteria

^c Both Cement Type and ASTM C1012 criteria govern

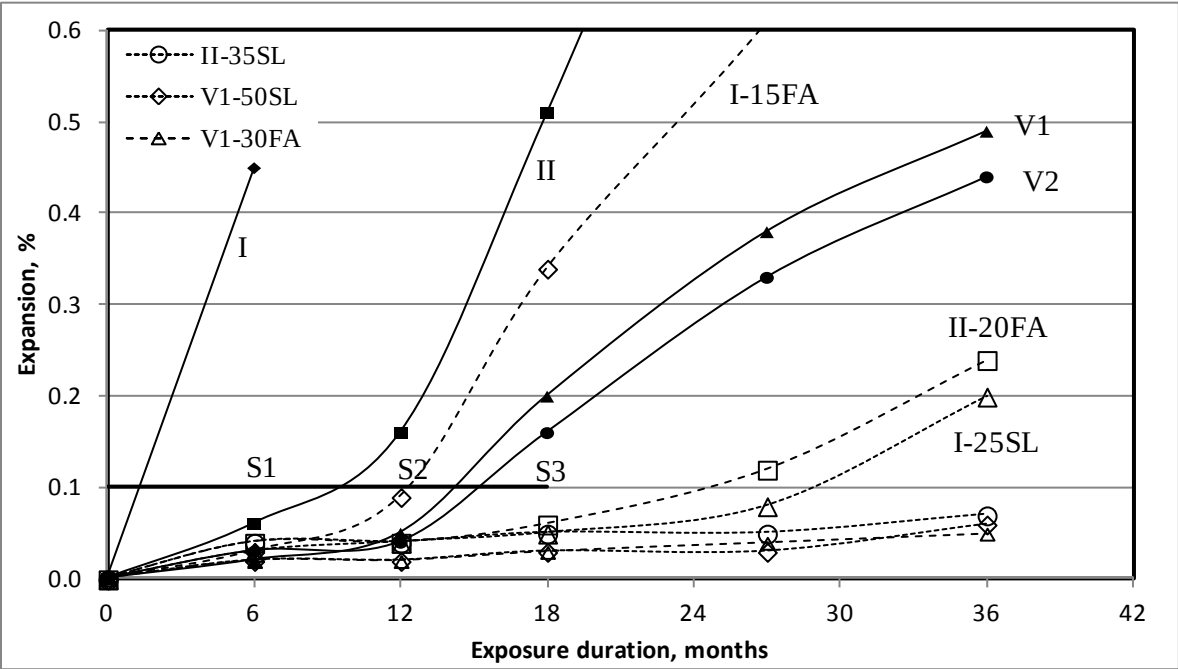


Figure 1 – ASTM C1012 Expansion Results for 10 Mortar Mixtures

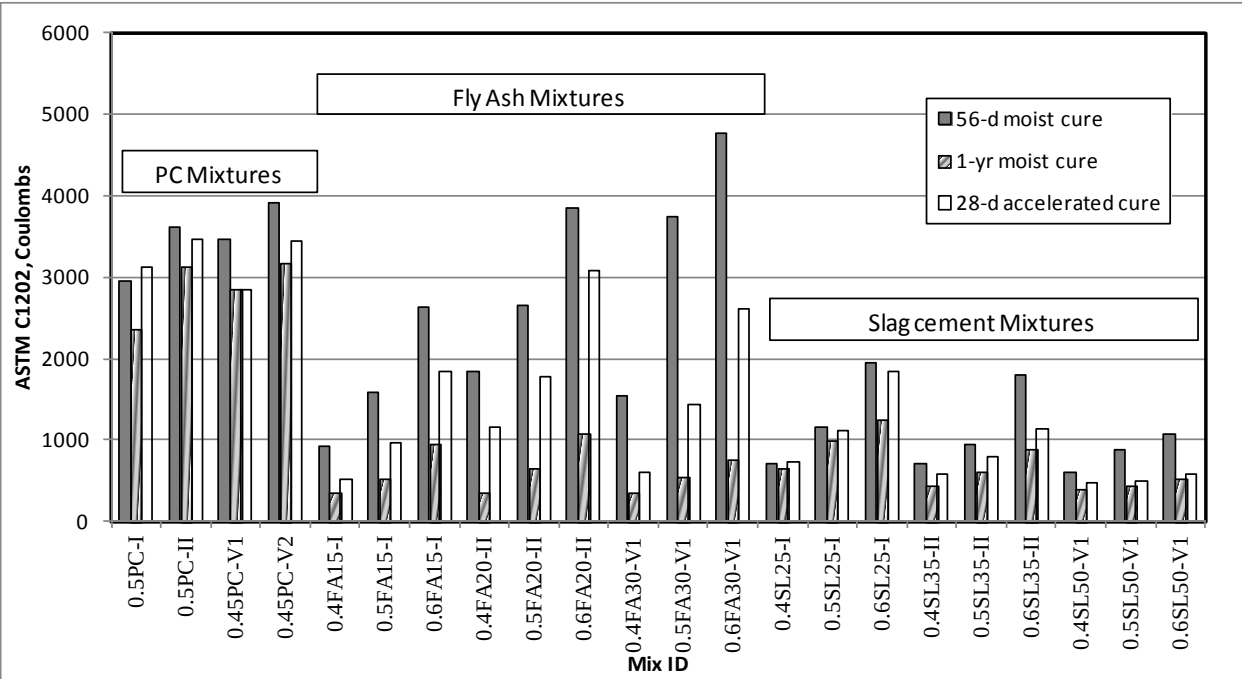


Figure 2 – ASTM C1202 (RCP) Results for Concrete Mixtures

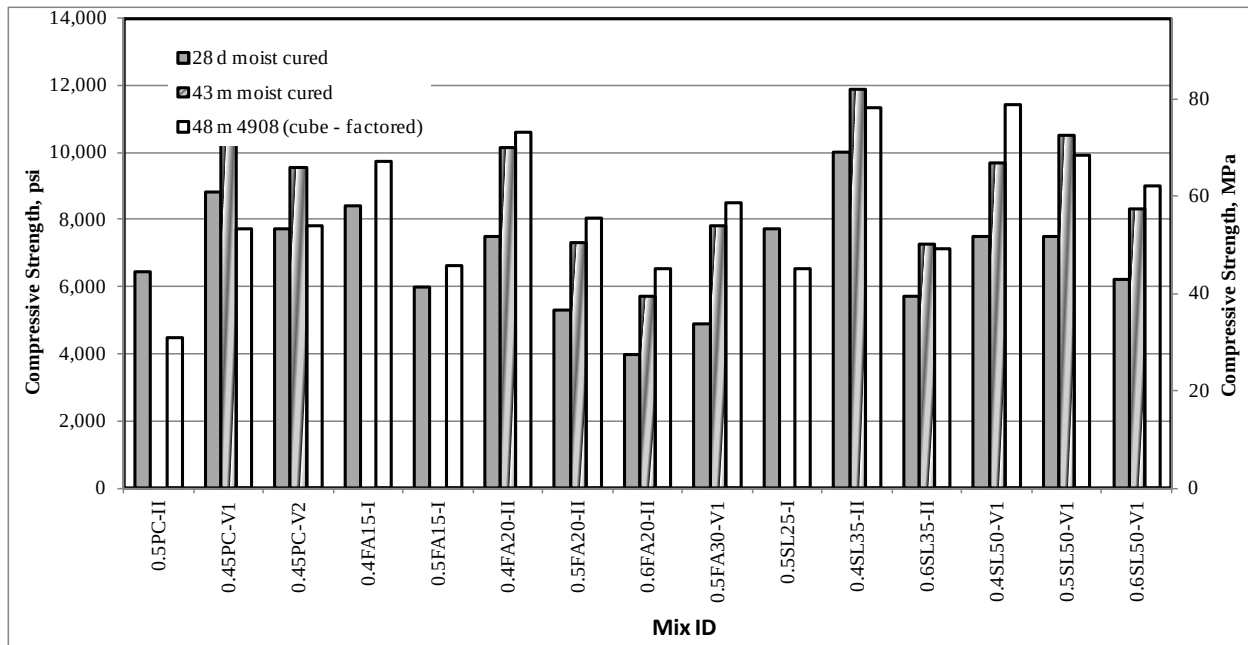


Figure 3 – Comparison of Strength of Concrete Mixtures – Standard-cured and Exposed to Sulfate

SULFATE RESISTANCE OF TERNARY BLEND CONCRETES: INFLUENCE OF BINDER COMPOSITION ON PERFORMANCE

R. Brett Holland, Kimberly E. Kurtis, Lawrence F. Kahn

SYNOPSIS: Due to the increasing costs of maintaining deteriorating infrastructure, there has been an increased importance placed on the durability of new concrete structures. For marine structures and structures constructed in sulfate rich soils, sulfate attack can cause the structure to degrade over time. Historically, sulfate attack resistance has been evaluated using an expansion test method. However, in addition to expansion during sulfate attack, concrete can exhibit strength degradation without expansion.

Resistance to sulfate attack was assessed using both expansion and strength degradation test methods for thirteen binder compositions. Results were compared to established criteria for expansion and proposed criteria for change in strength and were correlated to overall binder composition, considering the combination of three cement types and five supplementary cementitious materials (SCMs). Compressive strength degradation testing demonstrated that mix designs with a high initial CaO content, determined through oxide analysis of the cement and SCMs, performed well, presumably due to the formation of calcium hydroxide (CH) which served as a buffer to the decalcification of calcium-silicate-hydrate (C-S-H) in the formation of gypsum. However, high CaO contents led to poor performance on expansion testing due to the availability of large amounts of calcium hydroxide to react with sulfate ions to form expansive ettringite. Slag mix designs containing metakaolin performed well on both criteria.

Keywords: Sulfate Attack, Concrete Durability, Ternary Blend Concrete

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Introduction

Concrete structures can be exposed to high concentrations of sulfates through their interactions with seawater and brackish water, industrial and agricultural effluents, and through exposure to sulfate rich soils,. Damage to the concrete due various reactions between the external sources of sulfate ions and hydration products and anhydrous cement phases in the cement paste is termed “sulfate attack”. There are two primary mechanisms associated with sulfate attack. First, sulfate ions can react with monosulfo-aluminate or available tricalcium-aluminate (C_3A) to form ettringite, which can be expansive and can lead to cracking and spalling. Second, sulfate ions may react with available calcium hydroxide (CH) to form gypsum. If there is no CH present, then the calcium comes from the decomposition of the calcium silicate hydrate phase (C-S-H). The loss of calcium from the C-S-H leads to a reduction in strength (Skalny, et al., 2002). A thorough review of sulfate attack is found in Skalny, et al. (2002).

The concentration of sulfate ions has a large effect on the extent and rate of sulfate attack. ACI 201 (2010) provides guidelines for four exposure classes and requirements to protect against each level of exposure. Table 1 shows the requirements proposed by ACI 201 for a given sulfate exposure in water. The recommended cement type is based upon an ASTM C150 (2009) cement designation. Alternatively, the ASTM C 1157 (2011) performance based specification for cements can be used and requires testing following the ASTM C1012 (2009) procedure with expansion limits.

Table 1 - Exposure Classes as specified by ACI 201 (2010)

Exposure Class		Cement Type*	Exposure		Max w/cm
			% by mass	ppm	
S0	Not Applicable	No Restriction	$SO_4 < 0.10$	$SO_4 < 150$	None
S1	Moderate	Type II	$0.10 \leq SO_4 < 0.20$	$150 \leq SO_4 < 1,500$	0.5
S2	Severe	Type V	$0.20 \leq SO_4 < 2.0$	$1,500 \leq SO_4 < 10,000$	0.45
S3	Very Severe	Type V + Pozzolan or Slag	$SO_4 > 2.0$	$SO_4 > 10,000$	0.4

*Alternatively, any blend of portland cement of any type meeting ASTM C150 or C1157 with fly ash or natural pozzolan meeting ASTM C618, silica fume meeting ASTM C1240, or slag meeting ASTM C989 that meets the expansion requirements given in Table 4 when tested in accordance with ASTM C1012 may be used.

The ACI 201 (2010) approach relies upon the use of ASTM C1012 (2009) expansion tests. However, this test only accounts for one (i.e., expansion) of the two deleterious reactions associated with sulfate attack and may not provide a full characterization to a mix designs performance in a sulfate-laden environment. Compressive strength testing accounts for the deterioration of strength-giving calcium silicate hydrates to form gypsum, which is more commonly reported in field studies of sulfate damage. The ASTM C1012 (2009) test only accounts for the effects of ettringite formation in its expansion evaluation. Cracking caused by ettringite or gypsum formation and ettringite expansion, as well as C-S-H deterioration adversely affects the measured compressive strength, and, therefore, both primary reactions are accounted for when using a compressive strength testing methodology. In order to accurately characterize the sulfate resistance properties of a mix design, both the expansion and strength degradation reactions must be accounted for to assure satisfactory performance (Kurtis, et al. 2001; Mehta 1975).

For severe exposures, it has been shown (Mindess, et al., 2003) that the use of a sulfate resistant cement (ASTM C150 (2009) Type II or V) alone is not sufficient to prevent damage. The use of SCMs as a partial replacement of cement has been shown to produce large improvements in the resistance of binder compositions to sulfate attack (Kurtis, et al. 2001; Mindess, et al., 2003). There are two primary causes for the improvement of sulfate resistance by the use of SCMs. First, the “dilution effect” occurs since the addition of SCMs generally reduces the amount of C_3A present in the binder, which leads to less susceptibility to ettringite formation (Sideris, 2006). Second, the “pozzolanic effect” occurs when pozzolanic SCMs react with calcium hydroxide (CH) and water to produce secondary calcium-silicate-hydrate (C-S-H). The formation of secondary C-S-H increases the density of the hydrated cement paste by

filling capillary pores, which improves the strength and transport properties (Sideris, 2006). The “pozzolanic effect” occurs slowly, and the improvement in durability properties will only occur after adequate time has passed for the materials to react (Odler, 1997).

This research examines the sulfate resistance of binary and ternary blend binder compositions. As discussed above, previous research has shown that the use of sulfate resistant cements alone are not sufficient for aggressive sulfate environments, but binary and ternary blends have shown better long-term performance using expansion based criteria. However, the use of standard expansion based performance criteria does not account for both of the deleterious reactions associated with sulfate attack. In order to characterize the performance of binary and ternary blend binder compositions, we performed testing using both the traditional expansion based tests and strength-loss sulfate exposure testing. The objectives of our research were as follows:

- Assess the sulfate resistance of the different binder compositions by performing both expansion and compressive strength testing.
- Assess the impact of binder composition on the sulfate resistance performance in both expansion and compressive strength test results.
- Make recommendations about testing methodologies and appropriate binder compositions for sulfate resistance.

Experimental Program

The expansion and compressive strength behavior of thirteen binder compositions subjected to sulfate exposure were evaluated. The binder compositions evaluated are given in Table 2, and the oxide analyses of the cements and SCMs examined (i.e., fly ash, slag, silica fume and metakaolin) are provided in Table 3. The binder compositions are labeled with the notation of cement type and SCM – replacement level used, where the type of cement was denoted by T2, T3 or T5 for a Type II, Type III or V cement before listing the SCM’s present. SCM’s were abbreviated with the following notation: fly ash (F), slag (S), silica fume (SF), and metakaolin (MK). The fly ash conformed to ASTM C618 specifications for Class F. ASTM C150 (2009) Type II, III, and V cements were used for comparison with binary and ternary compositions containing SCM’s; each mixture was designed to increase sulfate resistance based upon previous research findings. SCM’s are given as a percent of total binder composition.

Table 2 - Binder compositions

Mix ID	Cement		SCMs (%) by mass			
	%	ASTM C150 Type	Fly Ash	Slag	Silica Fume	Metakaolin
T2	100	Type II	0	0	0	0
T3	100	Type III	0	0	0	0
T5	100	Type V	0	0	0	0
T3-F15	85	Type III	15	0	0	0
T2-F25	75	Type II	25	0	0	0
T2-F25-SF5	70	Type II	25	0	5	0
T2-F25-SF10	65	Type II	25	0	10	0
T2-F25-MK5	70	Type II	25	0	0	5
T2-F25-MK10	65	Type II	25	0	0	10
T2-S35-MK5	60	Type II	0	35	0	5
T2-S50-MK5	45	Type II	0	50	0	5
T2-S35-SF5	60	Type II	0	35	5	0
T2-S50-SF5	45	Type II	0	50	5	0

Table 3 - Oxide analysis and Bogue potential compositions of materials

Sample		Type II OPC	Type III OPC	Type V OPC	Fly Ash	Slag	Silica Fume	Metakaolin
SiO ₂	%	20.51	20.80	20.81	55.95	38.95	94.43	51.28
Al ₂ O ₃	%	4.65	4.96	4.30	29.39	8.04	0.37	44.27
Fe ₂ O ₃	%	3.35	3.30	4.14	4.91	0.41	0.09	0.40
CaO	%	62.60	63.74	63.52	1.05	37.23	0.59	0.08
MgO	%	2.81	1.06	1.40	0.86	12.10	0.37	0.17
SO ₃	%	2.99	3.46	2.55	0.29	1.83	0.16	0.13
LOI	%	1.85	1.50	2.08	2.69	-0.24	3.00	0.96
Na ₂ O	%	0.07	0.11	0.22	0.29	0.28	0.08	0.41
K ₂ O	%	0.75	0.53	0.44	2.16	0.42	0.68	0.11
TiO ₂	%	0.28	0.26	0.20	1.72	0.29	0.01	1.85
P ₂ O ₅	%	0.04	0.14	0.15	0.48	0.01	0.12	0.29
MnO	%	0.05	0.03	0.12	0.02	0.38	0.03	0.01
SrO	%	< 0.01	< 0.01	< 0.01	0.13	0.05	< 0.01	0.01
C ₃ S	%	54	54	58	-	-	-	-
C ₂ S	%	18	19	16	-	-	-	-
C ₃ A	%	6.7	7.6	4.4	-	-	-	-
C ₄ AF	%	10	10	13	-	-	-	-
Gypsum	%	6.4	7.5	5.5	-	-	-	-

The sulfate resistance of each mix design was investigated using two accelerated test methods. Accelerated expansion tests were performed in accordance with ASTM C1012 (2009) on mortar samples with the binder compositions given in Table 2 and compared against the expansion limits provided by ACI 201 (2010) for different exposure classes, as given in Table 4. Expansion tests were performed for eighteen months.

Table 4 - Maximum expansion percentages specified by ACI 201 (2010)

Exposure Class	Expansion (%)		
	6 Months	12 Months	18 Months
S1	0.10%	-	-
S2	0.50%	0.10%	-
S3	-	-	0.10%

Compressive strength testing was performed on paste cube samples by the method originally proposed by Mehta (1975). Paste cube samples (0.5 in, 13 mm) were cast simultaneously with ASTM C1012 (2009) samples using a 0.5 w/cm and cured in the molds for 24 hours and then moist cured for seven days at 122°F (50°C). After the curing period, samples were placed into a 4% Na₂SO₄ solution where the pH was maintained at 7.2 by autotitration with sulfuric acid at a molarity of 2.0. The small sample size, high surface area-to-volume ration, and high w/c increase the rate of interaction between the cement paste and sulfate solution (Mehta, 1975). By maintaining a constant pH, the effects of leaching of calcium hydroxide were minimized, and the environment better replicated field conditions. Through the use of sulfuric acid, Brown (1981) showed that the sulfate concentration remains constant. For each mix, the compressive strength of control and exposed samples were tested prior to the time of exposure, as well as, after twenty-eight, ninety, and 180 days of exposure. Eight samples with sulfate exposure and eight control samples were tested at each age at a load rate of 600 lb/min (2.7 kN/min)

Results and Discussion

The following sections present the results and discussion of our expansion and compressive strength testing for the thirteen binder compositions representing three types of ASTM C150 cements, and binary and ternary blends using fly ash, slag, silica fume, and metakaolin, as presented in Table 2. The testing considered the impact of different cement types, as well as SCM replacements in binary and ternary blends on their sulfate resistance, as measured by expansion and strength loss testing.

ASTM C1012 Expansion Testing

Figure 1 shows the expansion results for the ASTM C150 (2009) Type II, III, and V cements (T2, T3, and T5, respectively) and a dashed line gives the expansion limits, as presented in Table 4, for Exposure Classes S2 and S3. Testing was continued to eighteen months for comparison with the S3 eighteen month limit of 0.1% expansion to determine the adequacy of mix designs for more severe environments.

Only T3 failed the twelve-month limit, which was expected since both T2 and T5 binders contain low C_3A contents (<5%) and are ASTM C150 (2011) sulfate resistant cements. This suggests that an ASTM C150 (2011) Type III cement alone is not capable of providing adequate sulfate resistance in a sulfate rich environment consistent with an S2 and S3 exposure, but a Type II or V cement may be able to provide adequate resistance for an expansion-based criterion for an S2 exposure. T2 and T5 failed the eighteen-month limit at fourteen and thirteen months, respectively. The eighteen-month limit suggests that cements alone – even sulfate resistant cements – are not adequate for an S3 exposure severe sulfate rich environment, which is consistent with ACI 201's guidance. All three cements examined, however, met the less stringent six month 0.1% expansion limit and may perform adequately in less aggressive sulfate environments.

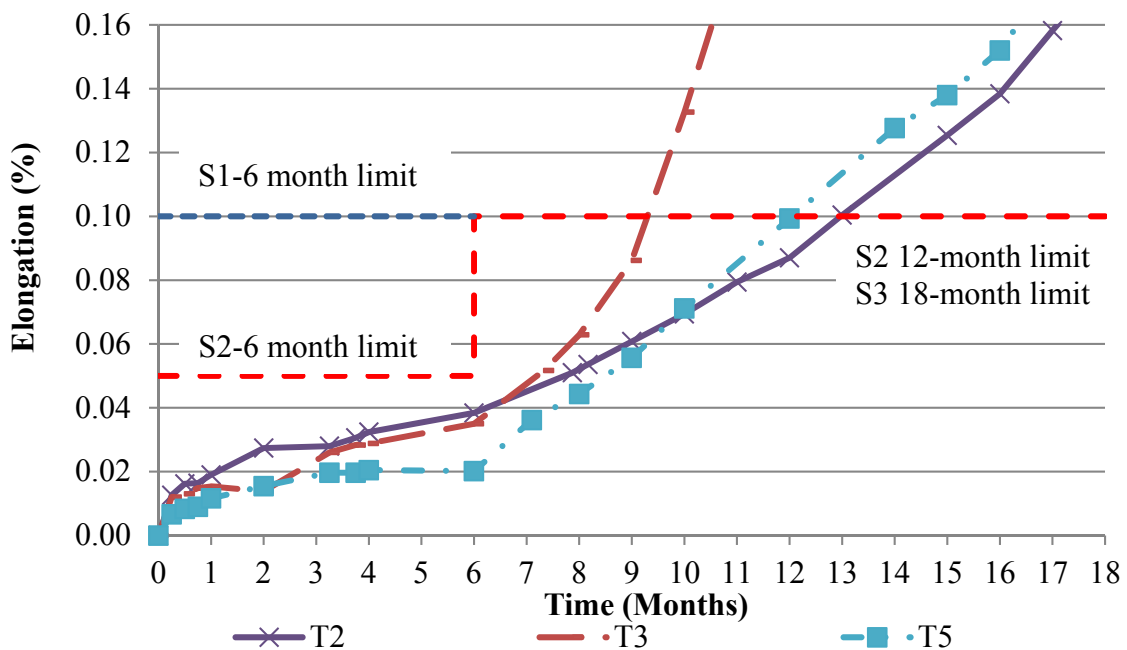


Figure 1 - ASTM C1012 expansion results for cement mixes.

Figures 2 and 3 show the expansion results for binder compositions containing fly ash and slag, respectively, with the dashed red line representing the expansion limits. All of the blended cement mix designs (T3-F15, T2-F25, T2-F25-MK5, T2-F25-MK10, T2-F25-SF5, T2-F25-SF10, T2-S35-MK5, T2-S50-MK5, T2-S35-SF5, and T2-S50-SF5) met the severe exposure (S2) expansion limits, which suggests that these mix designs possess adequate resistance to sulfate attack for moderate sulfate rich environments according to ACI 201. F25-MK5 failed the eighteen-month expansion limit, suggesting it provides lower

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sulfate resistance than the other ternary mix designs, but is still suitable for an S1 or S2 exposure environment.

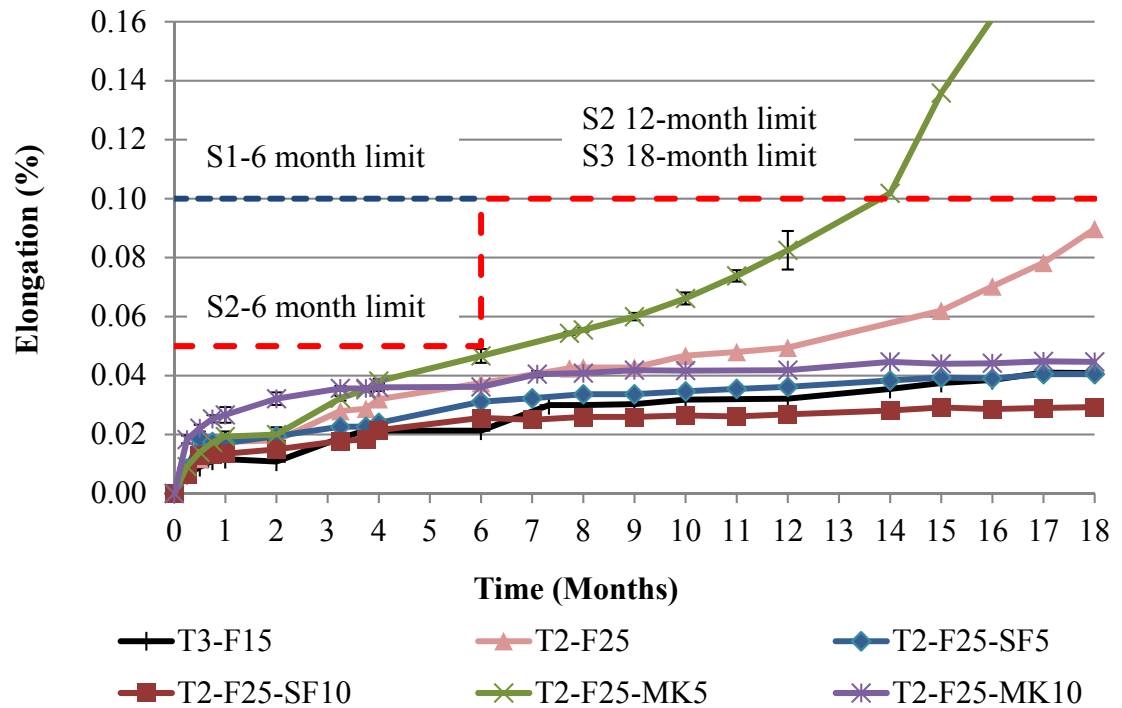


Figure 2 - ASTM C1012 expansion results for binder compositions containing fly ash.

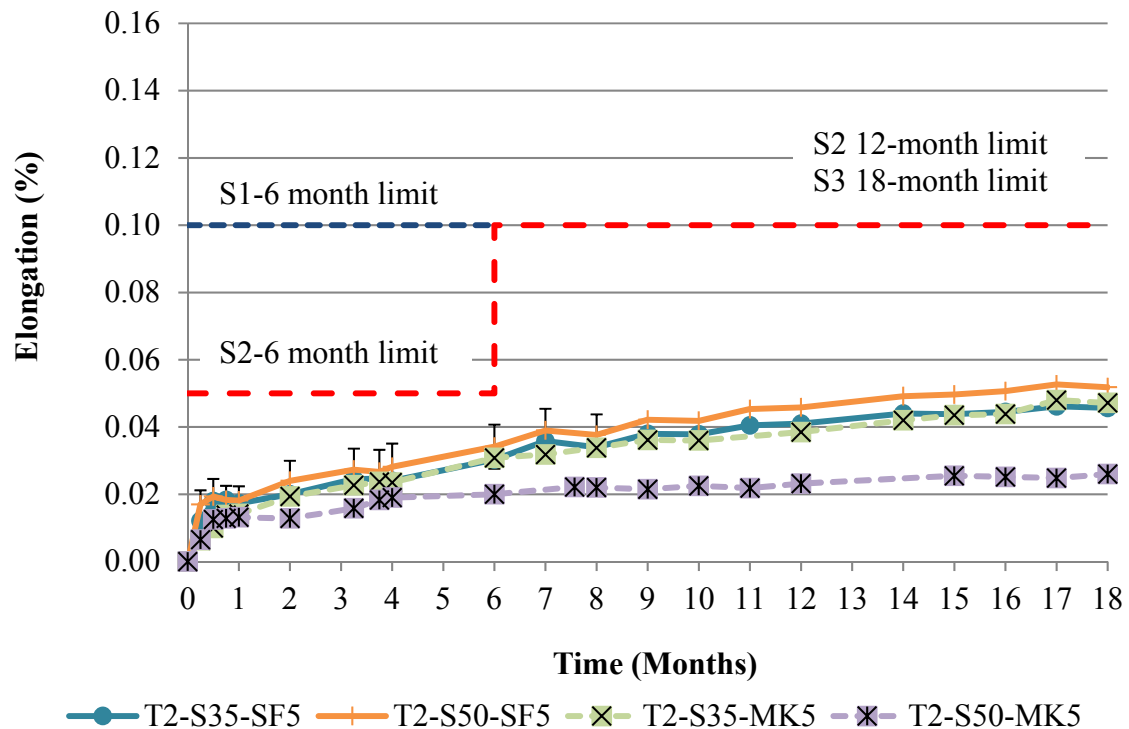


Figure 3 - ASTM C1012 expansion results for binder compositions containing slag.

The results of expansion testing have shown that any of the investigated binder compositions provide adequate sulfate resistance for an S1 environment. All binder compositions except for T3 demonstrated satisfactory sulfate resistance for S2 exposure classes and are suitable for use in moderate sulfate rich environments according to the ACI 201 (2010) expansion limits. All mix designs except cement only (T2, T3, and T5) and T2-F25-MK5 passed the eighteen-month S3 exposure condition. This suggests that any of these mix designs are capable of providing excellent sulfate resistance using the expansion failure criteria for an S1, S2, or S3 exposure environment. Mix design T2-F25 demonstrated an increasing rate of expansion leading up to the eighteen-month reading, and may not be as sulfate resistant as the other passing mix designs.

Compressive Strength Testing

The compressive strength testing was performed after 180 days of exposure to samples in a 5% sodium sulfate solution with a controlled pH. After the exposure period, varying degrees of visible damage were observed. Figure 4 shows a T5 control and sulfate exposure sample after 180 days. The sulfate exposure sample had cracking along the edges of the cube, but no spalling of corners or surfaces. In contrast, Figure 5 shows a T3 control and sulfate exposure sample. The sulfate exposure sample had extensive cracking and spalling of corners and edges.



Figure 4 - T5 180-day control (left) and sulfate (right) exposure 0.5 in. (12.7 mm) paste cube specimens.



Figure 5 - T3 180-day control (left) and sulfate (right) exposure 0.5 in. (12.7 mm) paste cube specimens.

The relative strength of each mix design compared to the control sample at the same age was calculated using Eq. 3 and plotted in Figure 6 for twenty-eight, ninety, and 180 days of exposure. The relative strength was determined using sulfate exposure sample strengths relative to the initial strength of the same mix design prior to exposure at 7-days of age, which is consistent with the test method described by Mehta (1975).

$$\text{Relative Strength (\%)} = \frac{\text{Sulfate Exposure Strength}}{\text{Initial Control Sample Strength}} \times 100 \quad (\text{Eq. 3})$$

Hypothesis testing was performed with an α of 0.05 for statistical equivalency of sulfate exposure specimens and control specimens. After twenty-eight days of exposure, no sulfate exposure samples showed statistically significant lower strengths than the control specimens of the same age. However, T2 sulfate exposure specimens showed a statistically significant higher strength than the control specimens. The increasing strength of the ASTM C150 (2011) Type II cement samples result matches the findings of Kurtis, et al. (2001).

After the ninety-day exposure period, the T3-F15, T2-F25-SF10, and T2-S50-SF5 mix designs showed statistically significant decreases in strength. T3-F15 showed the largest decrease in strength, with a 22% decrease in strength compared to the control specimens.

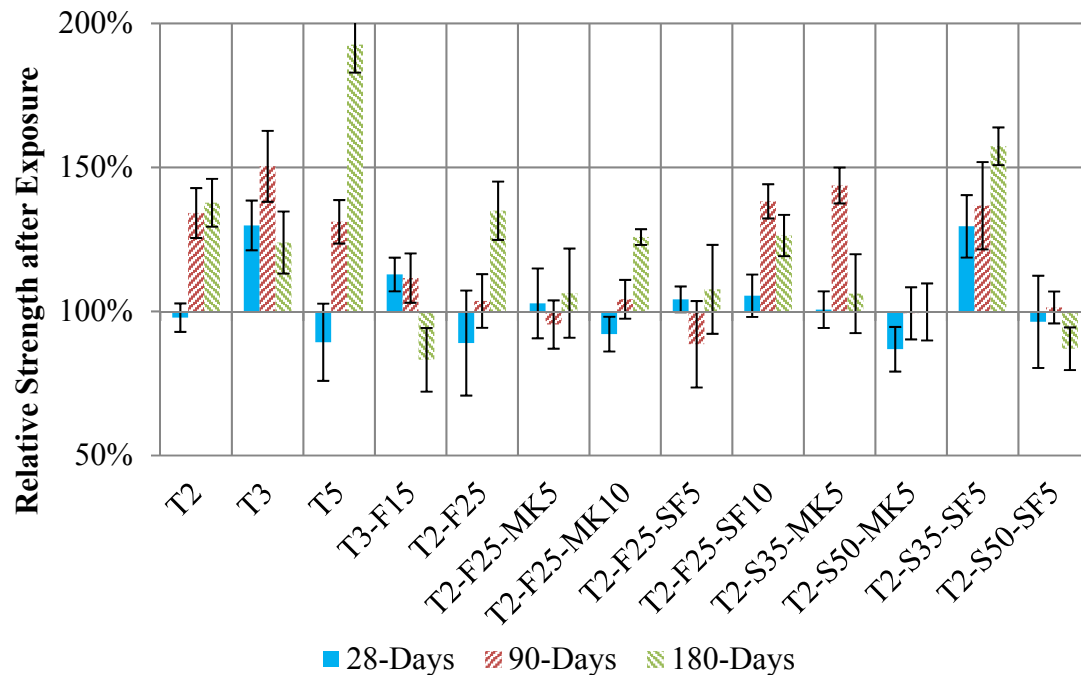


Figure 6 - Relative strength of sulfate exposure samples compared to the strength of control samples at start of test (seven days of age).

After the 180 day exposure period, the T3, T3-F15, T2-F25-SF10, T2-S35-SF5, and T2-S50-SF5 mix designs showed statistically significant decreases in strength. T3-F15 showed the largest decrease in strength, with a 42% decrease in strength compared to the control specimens. T2 and T5 demonstrated statistically significant higher strengths in sulfate exposure specimens than control specimens.

Limits given in Table 5 were used to evaluate the performance of binder compositions, where for each binder composition f_{c180} is the average 180 day compressive strength of sulfate exposure samples, σ_{180} is the standard deviation of the 180 day compressive strength sulfate exposure samples, and f_{ci} is the control compressive strength at the start of the test. The limits were proposed based upon the work of Kurtis (2001) and Cohen and Mather (1991) where it was identified that limits on the compressive strength degradation must be based upon strength loss, since cements will continue hydrating in the sulfate solution and may experience pore filling due to reaction with ingressing sulfates. Since both effects can result in strength gain, an increase in strength does not necessarily relate to improved sulfate resistance. Two criterion were chosen and placed varying levels of restriction upon the strength degradation behavior. First, for a severe sulfate exposure, S2, the 180-day compressive strength plus one standard deviation of sulfate exposure specimens must be higher than the initial strength. This limit accounts for the inherent variability with paste cube testing and any mix design demonstrating strength loss to below its initial strength will fail. For a very severe exposure, S3, the limit is that the 180 day compressive strength plus one standard deviation of sulfate exposure specimens must be higher than the ninety day compressive strength of sulfate exposure specimens. This enforces that a mix cannot exhibit a strength loss even after prolonged sulfate exposure. Additionally, this limit will minimize the influence of continued hydration through using strengths determined after ninety days of exposure.

Table 5 - Sulfate compressive strength degradation testing proposed limits

Exposure Class	Strength Limit
S1	-
S2	$f_{c180} + \sigma_{180} > f_{ci}$

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S3	$f_{c180} + \sigma_{180} > f_{c90}$
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Table 6 presents the exposure class rating for each mix design based upon compressive strength degradation criterion (as well as the expansion based criteria). For cement-only specimens, both T2 and T5 never exhibited strength loss with continued exposure to sulfates. T3 showed strength loss between ninety and 180 days. All fly ash mix designs showed a decreasing trend in strengths after the twenty-eight days of exposure. T3-F15 showed the largest decrease in strength. T3-F15 and T2-S50-SF5 failed the severe exposure limits, suggesting they are only suitable for a S1 sulfate exposure class. T3, T2-F25-SF10, and T2-S35-MK5 failed the S3 exposure limit, suggesting they are suitable for S1 or S2 exposure classes. The sulfate resistance cement only compositions (T2, T5) and T2-F25, T2-F25-MK5, T2-F25-MK10, T2-F25-SF5, T2-S50-MK5, and T2-S35-SF5 passed the S2 and S3 limits, and are suitable for any sulfate exposure using the strength degradation criterion.

Comparison of Expansion and Compressive Strength Data

The assessment of binder performance varied in some cases depending upon whether the ASTM C1012 (2009) expansion behavior or compressive strength was being considered. The variance in performance demonstrates that neither test alone is adequate for determining concrete performance in sulfate environments. The results suggest that both the ASTM C1012 (2009) and compressive strength testing should be used to test for sulfate attack resistance until a more comprehensive test method is developed that is capable of accounting for both degradation mechanisms.

Table 6 provides a summary of the strength and expansion test results, as well as an overall rating for sulfate resistance considering both of these criteria. Boxes highlighted in red represent a mix design suitable for Exposure Class S1, yellow for Exposure Class S2, and green for Exposure Class S3. When results from strength and expansion testing do not agree, the lower exposure class is assumed to govern predicted sulfate resistance. For example, while T2 and T5 performed the best on the strength testing, both however failed the eighteen-month limit for expansion testing and are rated for S2 environments. T3 performed poorly on both tests, which is to be expected since it was not designed for sulfate resistance. Slag mix designs containing metakaolin performed well with both test methods.

The testing performed to characterize the adequacy of mix designs for sulfate exposure only evaluated the effect of composition by using a high w/cm of 0.485 and 0.5 for expansion and compressive strength testing, respectively. Transport properties of mix designs also can help in sulfate resistance by limiting the rate of ingress of sulfates. From previous work by Holland (2012), it has been shown that the use of SCM's with a low w/cm greatly decreases the penetrability of concrete. Therefore, the use of a high sulfate resistance binder composition containing SCM's and a low w/cm is recommended.

Table 6 - Summary of sulfate testing results

Mix	ASTM C1012	Strength Degradation	Overall Exposure Rating
	Rating	Rating	
T2	S2	S3	S2
T3	S1	S2	S1
T5	S2	S3	S2
T3-F15	S3	S1	S1
T2-F25	S3	S3	S3
T2-F25-MK5	S2	S3	S2
T2-F25-MK10	S3	S3	S3

T2-F25-SF5	S3	S3	S3
T2-F25-SF10	S3	S2	S2
T2-S35-MK5	S3	S2	S2
T2-S50-MK5	S3	S3	S3
T2-S35-SF5	S3	S3	S3
T2-S50-SF5	S3	S1	S1

Conclusions and Recommendations

The results of this sulfate resistance study demonstrated that the measured performance varied for many binder compositions depending upon the measured property, i.e., change in strength or expansion. Based upon those test results, T2-F25-MK10, T2-F25-SF5, T2-S50-MK5 or T2-S35-SF5 are recommended for use in very severe (S3) sulfate rich environments. In general, expansion testing showed that cement only samples exhibited significantly higher expansion than SCM-containing compositions.

However, testing procedures that account for expansion and strength degradation should be used in developing high-performance concretes for sulfate rich environments. Testing for only one of the two degradation mechanisms will not guarantee adequate sulfate resistance for 100+ year service lives. These results then also highlight the need for research which correlates the measured expansion or compressive strength in an accelerated test method to field performance and service life modeling. Overall, these results demonstrate that both expansion and compressive strength testing should be performed to assess sulfate resistance until a more comprehensive test method is developed that is capable of accounting for both degradation mechanisms.

References

- ACI Committee 201 (2010). "ACI 201.2R-10 Guide to Durable Concrete," ACI Manual of Concrete Practice, ACI 201.2R-10, American Concrete Institute, Farmington Hills, MI.
- ASTM C150 (2009). "Standard Specification for Portland Cement," American Society for Testing and Materials, West Conshohocken, PA, pp. 10.
- ASTM C1012 (2009). "Standard Test Method for Length Change of Hydraulic-Cement Mortar Bars Exposed to a Sulfate Solution," American Society for Testing and Materials, West Conshohocken, PA, pp. 6.
- ASTM C 1157 (2004). "Standard Performance Specification for Hydraulic Cement," American Society for Testing and Materials, West Conshohocken, PA, pp. 5.
- Brown, P. (1981). "An Evaluation of the Sulfate Resistance of Cements in a Controlled Environment," Cement and Concrete Research, V. 11, pp. 719-727.
- Chang, C. F., and Chen, J. W. (2006). "The Experimental Investigation of Concrete Carbonation Depth," Cement and Concrete Research, V. 36 (9), pp. 1760-1767.
- Cohen, M. D. and Mather, B. (1991). "Sulfate attack on concrete— Research needs." ACI Materials Journal, V. 88, pp. 62– 69.
- Holland, R. (2012). Durability of Precast Prestressed Concrete Piles in Marine Environments. PhD Dissertation, Georgia Institute of Technology, U.S.A.
- Kurtis, K.E.; Shomglin, K.; Monteiro, P.; Harvey, J.; Roesler, J. (2001). "Accelerated Test for Measuring Sulfate Resistance of Calcium Sulfoaluminate, Calcium Aluminate, and Portland Cements," Journal of Materials in Civil Engineering, V. 13, pp. 216-221.

Sulfate Resistance of Ternary Blend Concretes: Influence of Binder Composition on Performance

Mehta, P.K. (1975). "Evaluation of Sulfate-resisting Cements by a New Test Method," Journal of ACI, V. 72, pp. 573–575.

Mindess, S.; Young, J.; Darwin, D. (2003). Concrete, 2nd Edition, Prentice Hall Publishers, Upper Saddle River, NJ.

Odler, I. (1997). "Ettringite Nomenclature (letter to editor)," Cement and Concrete Research, V. 27, E. 3, pp. 473-474.

Sideris, K.K.; Savva, A.; Papayianni, J. (2006). "Sulfate Resistance and Carbonation of Plain and Blended Cements," Cement and Concrete Composites, V. 28, pp. 47-56.

Skalny, J.; Marchand, J.; Odler, I. (2002). *Sulfate Attack on Concrete*, Spon Press, New York, NY, pp. 217.

Chemical and Mechanical Characterization of Damage Evolution in Concrete due to External Sulfate Attack

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Synopsis

External sulfate attack is often described by a diffusion–reaction mechanism which leads to the decomposition of hardened cement paste and cracking of concrete. In most studies, the linear expansion of mortar/concrete prisms is measured according to ASTM C1012. Even though this test can be used to determine the suitability of a mixture for specific sulfate exposure conditions, it does not provide insights on the actual degradation process. This paper presents a series of experiments performed to quantify the damage evolution on cement-based mortars with and without fly ash. Conventional expansion tests were conducted, followed by measuring the chemical and mechanical changes on the cross section of the specimens using EDS and microhardness techniques. The overall damage was further evaluated using a novel flexural fracture test on the specimens. It was observed that partial replacement of cement with class F fly ash reduced the level of mechanical damage in exposure to sulfate attack.

Keywords: cement, chemical analysis, damage, expansion, fly ash, fracture, sulfate attack

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INTRODUCTION

External sulfate attack is a phenomenon that may cause gradual but severe damage to concrete structures. Foundations, footers, piers, and slabs-on-ground are among concrete elements that are exposed to soil and may experience sulfate attack. The sulfates ions, brought to the concrete by the underground water, can diffuse in to the concrete, gradually interact with cement components, and cause degradation of hardened concrete [1]. The failure mechanisms are associated with various physical and chemical processes [2]. External sulfate attack using linear expansion measurements has been studied since 1930's by Tuthill [3] who noticed deteriorations in concrete structures caused by sulfate-bearing soils along the Colorado River. He used sodium sulfate solution to expose concrete prisms and measured the expansion values. Brown [4] in 1980's reported that a pH-constant solution represents the field conditions better, leading to much faster expansion of mortar bars than a typical non-controlled pH solution. This effect was further studied by Ferraris et al. [5] and Kurtis et al. [6] while the effect of solution concentration and type was addressed by various researchers including Lee et al. [7] and Santhanam et al. [8, 9] who reported faster expansion for MgSO_4 compared to Na_2SO_4 .

The test method known as ASTM C 1012 [10] uses mortar bars of $25 \times 25 \times 280$ mm ($1 \times 1 \times 11.2$ inch) in size that are exposed to 5% (50 g/L) sodium sulfate (Na_2SO_4) or magnesium sulfate (MgSO_4) solution with pH of 6-8, while length change measurement is carried out periodically up to 6 (or 12) months. Ferraris et al. [11] and Mobasher et al. [12] studied the specimen size effect showing that smaller prisms of $10 \times 10 \times 100$ mm ($0.4 \times 0.4 \times 4$ inch) in size will increase expansion rate, enhancing the test results in much less time than the standard size specimens. **Figure 1** shows the development of visible cracks in a typical standard size specimen exposed to external sulfate attack. Many of the internal damage parameters are however not visible to the naked eye and would have to be characterized by more sensitive techniques.

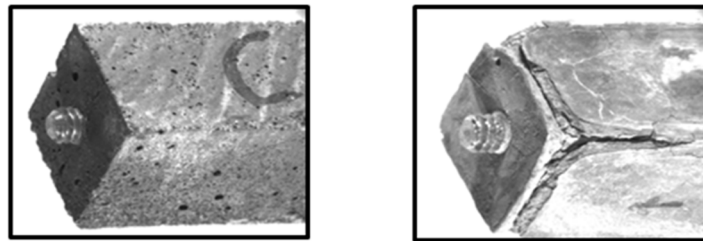


Figure 1. Development of cracks in a typical standard size $25 \times 25 \times 280$ mm ($1 \times 1 \times 11.2$ inch) specimen exposed to external sulfate attack

In external sulfate attack, the migration of sulfate ions in to concrete can be accompanied by a gradual dissolution of portlandite (CH) and decomposition of the C-S-H phase. In the latter case, the CaO/SiO_2 ratio of this phase eventually declines as increasing amounts of Ca^{2+} are removed from the structure, thus resulting in a strength loss of the hardened cement paste [13]. Simultaneously, the formation of ettringite crystals and consequent volumetric changes in the hardened material may result in expansive stresses and microcracking [14]. Atkinson and Hearne [15] were among the first researchers who predicted the degradation zone based on C_3A content and the molar concentration of Mg or SO_4 ions in the solution. Shuman et al. [16] included the effect of apparent diffusion coefficient while Kurtis et al. [17] and Monteiro and Kurtis [18] empirically predicted the expansion of cylindrical specimens based on W/C ratio as well as C_3A , C_3S , and C_4AF contents of the cement.

The approach by Atkinson and Hearne [19] models the ingress of sulfate ions in to concrete by the diffusion mechanism, followed by subsequent reaction with aluminates. This results in the formation of expansive crystals and cracking due to low fracture energy of concrete. Krajcinovic et al [20], Tixier and Mobasher [21] and more recently Basista and Weglewski [22] modeled the general microcracking of brittle materials caused from the diffusion of aggressive species and coupled reactions. Other mechanism-based models on the basis of diffusion-reaction and corresponding damage evolution have been proposed by Clifton and Pommersheim [23] and Gospodinov et al. [24, 25]. The effect of cracking on the rate of diffusion and expansion was modeled by Tixier and Mobasher [21], Gerard et al [26] and Gerard, Marchand [27].

The effectiveness of pozzolanic materials such as fly ash, silica fume, slag, and metakaolin in mitigating sulfate attack is well known and recognized by ACI 201 on concrete durability [28]. These materials are typically higher in SiO_2 and Al_2O_3 and lower in CaO contents compared to portland cement. They improve the microstructure of concrete and change the chemical behavior of the hydration products due to the particle size and reactivity with calcium hydroxide (CH). The reactivity controls how much portlandite (CH) can be converted to C-S-H gel which is the main source for strength [29]. Reduced ionic diffusivity and decreased C_3A availability are the major reasons that improve the sulfate resistance in blended cements using fly ash. A key factor why Class F fly ash is mainly used to mitigate sulfate attack is due to their much lower CaO content compared to class C.

Previous work by the author [30] showed that the expansion magnitude is dependent on the size of the specimen; therefore correlation of the expansion-durability correlation requires a model for transferring the experimental results in to viable design criteria. Prisms of standard size $25 \times 25 \times 285$ mm ($1 \times 1 \times 11.2$ inch) and modified smaller size $10 \times 10 \times 100$ mm ($0.4 \times 0.4 \times 4$ inch) were tested for testing sulfate attack using various mixtures. Individual expansion curves were plotted for these specimens and the individual data points were used in order to find a correlation between the expansion magnitudes in standard and smaller specimens. **Figure 2** shows two sets of correlations: one is a linear fit to the first 3 months of expansion data points; this is the time in which smaller specimens started cracking. A second line is fitted to the expansion data between 3 and 12 months of exposure with higher scatter because of the cracking in smaller specimens. The normalization factor between the expansion values in standard size and smaller size specimens used for plotting was 2.5. This number is the ratio of the surface area to the volume of each individual specimen. The higher the surface area, the more sulfate ions can diffuse in to the specimen, resulting in more expansion. One can see that the initial part is a one-to-one linear relationship while the linear fit to the final data points has a slope of 1.8 which is related to higher diffusion within the small specimen and cracking. It was found that when smaller specimens are used, the expansion test can be conducted only for 3 months, compared to 6-12 months typical measurement time for standard specimens.

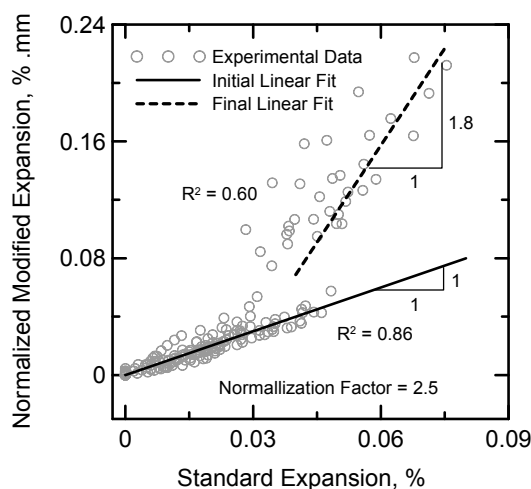


Figure 2. Comparison of standard and normalized modified expansion

Although ASTM C1012 can be used to determine the suitability of a mixture with supplementary cementitious materials for specific sulfate exposure conditions, it does not show the actual degradation process. This paper presents a series of experiments to further evaluate the damage process. Portland cement mixtures and blended cement mixtures (using class F fly ash) were used. Conventional expansion tests were conducted, followed by measuring the chemical and mechanical changes on the cross section of the specimens using EDS (Energy Dispersive Spectrometry) and microhardness techniques, respectively. Some part of this research has already been published by the authors [31] with an emphasis on the chemical alterations. The current paper, however, focuses on the mechanical changes in the sulfate attack process. The overall mechanical damage was further determined using flexural fracture tests. Application of fracture testing for evaluating the degradation of mechanical properties in sulfate attack is presented as a novel technique.

METHODS

The chemical compositions of the portland cement and the class F fly ash used in this study are shown in **Table 1** while the mixture proportions are presented in **Table 2**. The replacement level is approximately 30% by weight of cement. The linear expansions were measured according to ASTM C 1012 using digital comparators up to 18 months. Four replicate bar specimens were used for each mixture and the average values are reported.

Table 1: Chemical composition of cementitious materials

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I	Class
Cement	21.6	4.06	3.54	63.90	1.40	2.81	0.06	0.54	1.42	I/II
Fly Ash	58.72	24.86	4.94	4.56	1.57	0.21	1.11	1.11	0.25	F

Table 2: Mixture proportions for mortar mixes

Sample Code	Control	Blended
Cement, kg/m³ (lb/yd³)	700 (1,190)	500 (850)
Fine Aggregates, kg/m³ (lb/yd³)	1400 (2,380)	1400 (2,390)
Water, kg/m³ (lb/yd³)	350 (595)	350 (595)
Class F Fly Ash, kg/m³ (lb/yd³)	0.0 (0.0)	200 (340)
W/CM	0.50	0.50

Quantitative compositional analyses of exposed specimens were performed using window scanning option with an area of 1mm² for each grid point. A total number of 25 grid points were used for scanning the section. The standard size specimens used for the expansion test were also used for scanning electron microscopy (SEM) and chemical analysis using quantitative energy dispersive spectroscopy (EDS). Thin 25×25×10 mm (1×1×0.4 inch) sections were cut from the original specimens exposed to Na₂SO₄ solution as shown in **Figure 3**. The specimens were polished using 300 and 600 grit polishing papers and coated for SEM/EDS equipment shown in **Figure 4**. The thin section was scanned to obtain the 2D distribution (contour) of various chemical on the cross section.

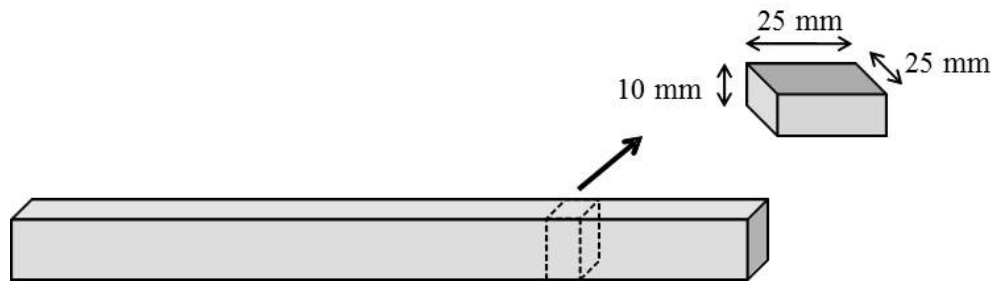


Figure 3. Specimen preparation for SEM and EDS (Note: 25 mm = 1 inch)



Figure 4. Equipment used for electron microscopy (SEM) and chemical analysis (EDS)

The $25 \times 25 \times 10$ mm ($1 \times 1 \times 0.4$ inch) thin specimens were also used for microhardness testing to understand the mechanical changes on the exposed samples. Micro-indentation is a common method of evaluating the quality of materials for engineering purposes, in particular ductile materials (i.e., metals) but also brittle materials such as ceramics and concrete [32]. This technique is based on applying a static load for a known period of time on the material surface and measuring the response in terms of size of indentation. The value is then used to determine the hardness of the material. The same 25 grid points were used for indentation. For each loading point, three replicate indentations were made and the average values were used for calculating the hardness values. **Figure 5** shows the macroscopic and microscopic images of a typical micro-indentation.

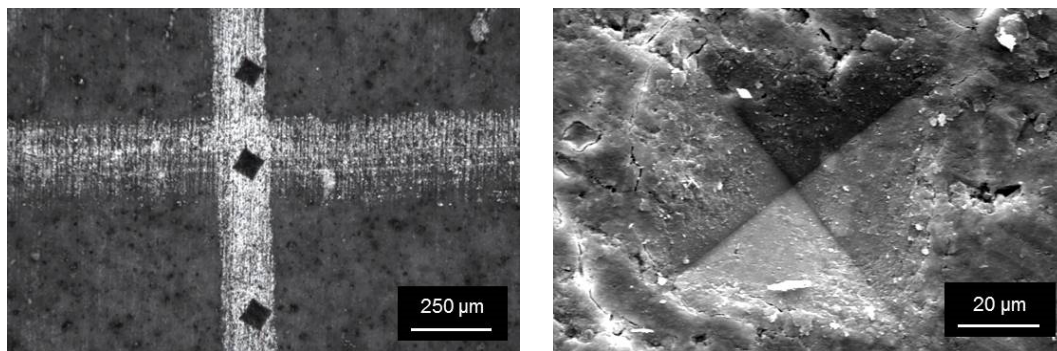


Figure 5. Typical micro-indentation images for hardness test

Mechanical damage and stiffness loss from sulfate attack is a major parameter in modeling sulfate attack. Therefore, measuring the flexural response of mortar/concrete specimens exposed to sodium sulfate can reveal important information on the degradation process. Flexural fatigue tests were performed to study the mechanical damage in specimens exposed to sulfate attack. The standard size mortar prisms that were subjected to sulfate exposure were used for this purpose. After 3, 6 and 12 months of exposure, these specimens were tested under closed-loop monotonic three-point flexural test. Two smaller prisms of $25 \times 25 \times 140$ mm ($1 \times 1 \times 5.6$ inch) in size were cut from each original specimen. A small notch (2 mm) was cut at the mid-span to initiate the crack in the three point bending test. A clip-gage (extensometer) was used for instrumentation of the test which was conducted under Crack Mouth Opening Displacement (CMOD) control as shown in **Figure 6**.

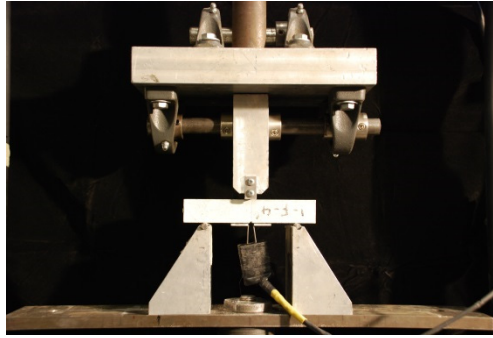


Figure 6. Three-point flexural fatigue test for specimens exposed to sulfate attack

RESULTS

The linear expansion of standard size bars were measured according to ASTM C1012 for control and blended mixtures, shown in **Figure 7**. Each curve shows the average values for four replicate specimens. After 6 months of exposure, the control and blended mixtures showed average expansion of about 0.1% and 0.07%, respectively. These values increase to about 0.4% and 0.1% after 12 months exposure. The control specimens showed excessive cracking and visual damage, hence, measurement of expansion was abandoned after 400 days of exposure. The blended mixture with class F fly ash did not show any visual cracking and the expansion measurement continued up to 18 months.

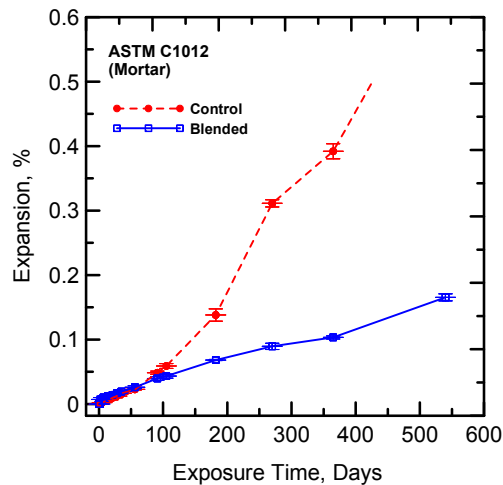


Figure 7. Linear expansion test results for mortar mixtures (control and blended with 30% class F fly ash)

The chemical composition of the exposed specimens were determined using scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS) tool. The area of $25 \times 25 \times 10$ mm ($1 \times 1 \times 0.4$ inch) sections was scanned and contours of chemical compositions were plotted. **Figure 8** shows the contour plots for sulfur and sodium elements, demonstrating the diffusion of these elements in to the specimen. **Figure 9**, however, shows the leaching of calcium and silicon outside of these specimens. The non-symmetrical distribution of these elements can be attributed to the possible cracking of the sample from the bottom surface and higher diffusion of S and Na, as well as higher leaching of Ca and Si from this surface. The coefficients of diffusion for sulfate ions measured from these experiments were approximately 2.4×10^{-11} and 1.4×10^{-11} m²/s for the control and blended mortar mixtures, respectively.

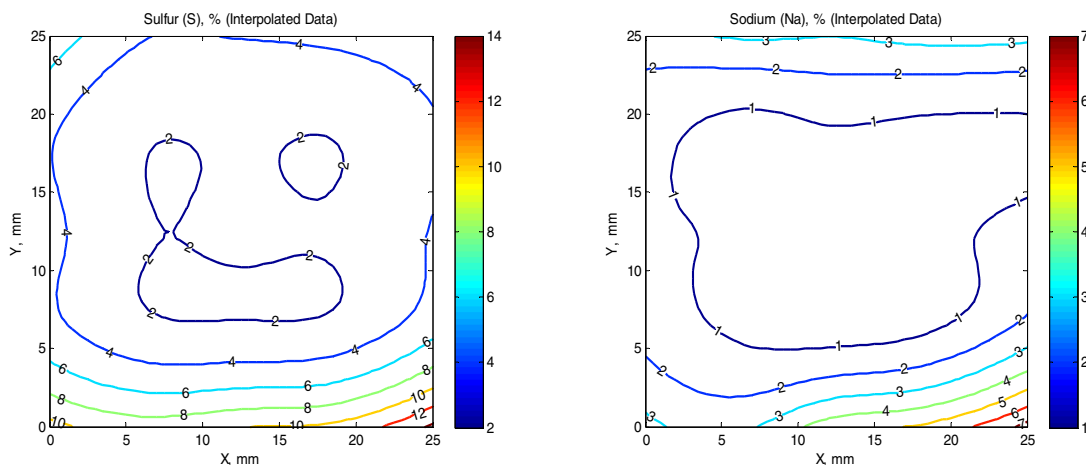


Figure 8. Contour of chemical compositions for sulfur and sodium (diffusion in to concrete)

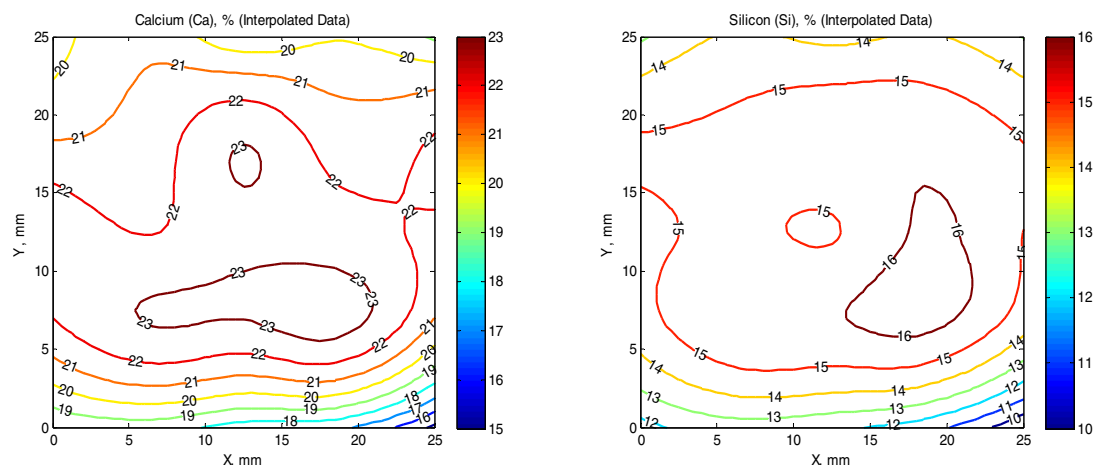


Figure 9. Contour of chemical compositions for calcium and silicon (leaching outside of concrete)

The values for microhardness were calculated for the thin sections using micro-indentation. The hardness decreases as the diffusion process proceeds in the cracked samples. This reduction is much higher in the control specimen (11.8%) compared to blended mixture (1.6%) after 12 months of exposure, presented in **Table 3**. In this table, ΔH is the change in hardness value from the exterior surfaces to the interior areas. The hardness values are interpolated and represented as contours shown in **Figure 10**.

Table 3: Hardness values and their changes specimens exposed to sulfate attack

Mixture	Location	Mortar
		12 Months
Control	Exterior surfaces	0.491±0.110
	Interior area	0.557±0.109
	ΔH (%)	-11.8%
Blended	Exterior surfaces	0.485±0.091
	Interior area	0.493±0.093
	ΔH (%)	-1.6%

Chemical and Mechanical Characterization of Damage Evolution in Concrete Due to External Sulfate Attack

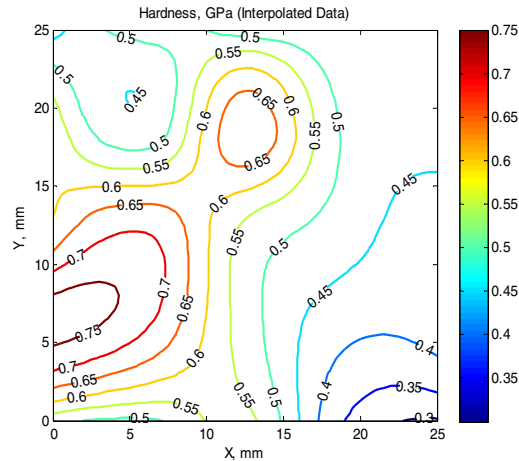


Figure 10. Hardness contour plots for control mortar after 12 months

The prisms exposed to sulfate solution were also used for measuring the flexural/fracture response. The specimens were cut in to smaller bars of $25 \times 25 \times 140$ mm ($1 \times 1 \times 5.6$ inch) in size with small notch of 2 mm (0.08 inch) in length as a crack initiator. A closed-loop test was performed with crack mouth opening displacement (CMOD) as the controlling signal and the load vs crack opening graphs were obtained. **Figure 11** shows the results for monotonic flexural test on these specimens for control and blended mortars with various exposure times. Compared to the blended mixtures, the control specimens started with a higher strength after curing and prior to exposure to sulfate solution. This is due to the slower rate of hydration reactions in the fly ash blended mixtures. After 3 months of exposure, the control specimens showed slight decrease in strength and stiffness, while the blended mixtures continued in gaining strength due to further hydration. After 12 months of exposure, the modulus of rupture (MOR) and stiffness (E) decreased to 62% and 82%, respectively in the control specimens. In the case of blended mixtures, the MOR reduced only to 90% while the stiffness (E) increased to 1.74 times the initial stiffness. As noted before, the blended mixture specimens did not have any visible cracking or damage as the sulfate attack was mitigated by fly ash. Comparing the post-crack performance of these small bars indicates that the control mixture showed a higher energy absorption which can be attributed to microcrack coalescence and higher fracture surface area. The blended mixture showed higher stiffness, hence more brittle behavior in the post-crack region.

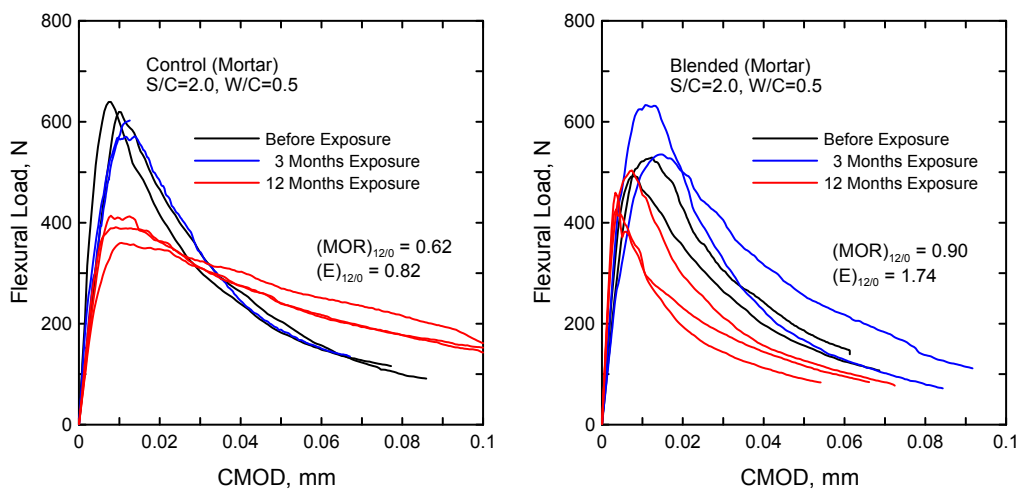


Figure 11. Flexural fracture test results for specimens exposed to sulfate attack and the ratios of MOR and E changes in control and blended mixtures. (Note: 25 mm = 1 inch)

CONCLUSIONS

The damage evolution in blended cement mortars was studied in exposure to external sulfate attack. Standard ASTM C1012 specimens were prepared and tested for linear expansion. Additional experiments were performed on the same specimens to better understand the degradation process caused by sulfate attack. The standard test method ASTM C1012, while suitable as an easy test for comparing the expansion and overall behavior of materials to sulfate attack, does not provide any quantitative information on the actual damage process. The chemical and mechanical changes on the cross section of the specimens were quantitatively measured using EDS and microhardness techniques, respectively. The plotted contours showed the diffusion of sulfate ions in to and leaching of calcium ions out of the specimens. The hardness of the materials in the diffusion zones was degraded much higher in the control specimen compared to the blended mixture. Furthermore, the overall mechanical damage was determined using flexural fracture tests on the same specimens. The application of this technique was novel with respect to studying sulfate attack. The mechanical degradation, expressed in terms of decrease in the modulus of rupture and stiffness was quantified. Both microhardness and fracture tests provided valuable insight about the mechanical properties and their changes in the sulfate attack process. For future studies, it is suggested that more number of these standard specimens be used for testing with various mix designs and raw materials. Higher number of specimens will provide a better understanding of the data variability. Specific mixture proportions and fly ash products can be used to extend the life of a concrete structure exposed to external sulfate attack.

REFERENCES

1. Bonakdar, A., Mobasher, B, "Multi-Parameter Study of External Sulfate Attack in Blended Cements", Construction and Building Materials, Vol. 24, 2010, pp. 61-70.
2. RILEM Report 12 (1995), "Performance Criteria for Concrete Durability", edited by J. Kropp and H. K. Hilsdorf, E & FN SPON.
3. Tuthill, L. H., "Resistance of Cement to the Corrosive Action of Sodium Sulfate Solutions", ACI Journal, Vol. 33, 1936, pp. 83-103.
4. Brown, P. W., "An Evaluation of the Sulfate Resistance of Cement in a Controlled Environment", Cement and Concrete Research, Vol. 11, 1981, pp. 719-727.
5. Ferraris, C. F., Clifton, J. R., Stutzman, P. E., Garboczi, E. J., "Mechanisms of Degradation of Portland Cement-Based Systems by Sulfate Attack", in Mechanisms of Chemical Degradation of Cement-Based Systems, Edited by: K. L. Scrivener and J. F. Young, E&FN Spon, London, 1997.
6. Kurtis, K. E., Shomglin, K., Monteiro, P. M., Harvey, J., Roesler, J., "Accelerated Test for Measuring Sulfate Resistance of Calcium Sulfoaluminate, Calcium Aluminate, and Portland Cements", Journal of Materials in Civil Engineering, 2001, pp. 216-221.
7. Lee, S. T., Moon, H. Y., Hooton, R. D., Kim, J. P., "Effect of Solution Concentrations and Replacement Levels of Metakaolin on the Resistance of Mortars Exposed to Magnesium Sulfate Solutions", Cement and Concrete Research, Vol. 35, 2005, pp. 1314-1323.
8. Santhanam, M., Cohen, M. D., Olek J., "Mechanism of Sulfate Attack: A Fresh Look Part 1: Summary of Experimental Results", Cement and Concrete Research, Vol. 32, 2002, pp. 915-921.
9. Santhanam, M., Cohen, M. D., Olek, J., "Modeling the Effects of Solution Temperature and Concentration During Sulfate Attack on Cement Mortars", Cement and Concrete Research, Vol. 32, 2002, pp. 585-592.
10. ASTM C 1012 (2004). "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution", American Society for Testing and Materials.
11. Ferraris, C., Stutzman, P., Peltz, M., Winpiger, J., "Developing a More Rapid Test to Assess Sulfate Resistance of Hydraulic Cements", Journal of Research of the National Institute of Standards and Technology, Vol. 110, No. 5, 2005, pp. 529-540.

12. Mobasher, B., Bonakdar, A., Anantharaman, S., "Modeling of Sulfate Resistance of Fly Ash Blended Cement Concrete Materials", Proceeding of World of Coal Ash, May 7-10, Kentucky, 2007.
13. Tixier, R., Mobasher, B., "Modeling of Damage in Cement-Based Materials Subjected To External Sulfate Attack- Part 2: Comparison with Experiments", ASCE Journal of Materials Engineering, Vol.15, No. 4, 2003, pp. 314-322.
14. Clifton, J. R., Ponneshheim, J. M., "Sulfate Attack of Cementitious Materials: Volumetric Relations and Expansions", NIST IR 5390, Gaithersburg, Maryland, 1994.
15. Atkinson A, Hearne J A. An assessment of the long-term durability of concrete in radioactive waste repositories. AERE-R11265, Harwell, UK, 1984.
16. Shuman R, Rogers V V, Shaw R A. The barrier code for predicting long-term concrete performance. Waste Management, University of Arizona, 1989.
17. Kurtis K E, Monteiro P J M, Madanat S. Empirical models to predict concrete expansion caused by sulfate attack. ACI Mater J 2000; 79: 156-161.
18. Monteiro P J M, Kurtis K E. Experimental asymptotic analysis of expansion of concrete exposed to sulfate attack. ACI Mater J 2008; 105: 62-71.
19. Atkinson A, Hearne J A. Mechanistic model for the durability of concrete barriers exposed to sulfate-bearing groundwater, Proceeding of Materials Research Society Symposium 176, 1990. p. 149-156.
20. Krajcinovic D, Basista M, Malliek K, Sumarac D. Chemo-Micromechanics of brittle solids. J Mech Phys Solids 1992; 40(5): 965-990.
21. Tixier, R., Mobasher, B., "Modeling of Damage in Cement-Based Materials Subjected To External Sulfate Attack- Part 1: Part 1: Formulation", ASCE Journal of Materials Engineering, Vol. 15, No. 4, pp 305-313, July/August 2003.
22. Basista M, Weglewski W. Chemically assisted damage of concrete: a model of expansion under external sulfate attack. Int J Damage Mech 2009; 18(1): 155-175.
23. Clifton J R, Ponneshheim J M. Sulfate attack of cementitious materials: volumetric relations and expansions. NIST IR 5390, Gaithersburg, MD, 1994.
24. Gospodinovic P, Kazandjiev R, Mironova M. Effect of sulfate ion diffusion on the structure of cement stone. Cem Concr Compos 1996; 18(6), 401-407.
25. Gospodinovic P, Kazandjiev R, Partalin T A, Mironova M. Diffusion of sulfate ions into cement stone regarding simultaneous chemical reactions and resulting effects. Cem Concr Res 1999; 29(10):1591-1596.
26. Gerard B, Pijaudier-Cabot G, Laborderie C. Coupled diffusion-damage modeling and the implications on failure due to strain localization. Int J Solids Struct 1998; 35(31): 4107-4120.
27. Gerard B, Marchand J. Influence of cracking on the diffusion properties of cement-based materials, part 1: influence of continuous cracks on the steady-state regime. Cem Concr Res 2000; 30: 37-43/
28. ACI 201.2R (2001), "Guide to Durable Concrete", American Concrete Institute.
29. Bentz, D. P. and Garbicz, E. J. (1991), "Simulation Studies of the Effects of Mineral Admixtures on the Cement Paste Aggregate Interfacial Zone", ACI Materials Journal, Vol. 88, No. 5, pp. 518-529.
30. Bonakdar, A., "Multi-Scale Study of Durability in Cement-Based Materials", PhD Dissertation, 2010, Arizona State University, Tempe, Arizona, USA.
31. Bonakdar, A., Mobasher, B., Chawla, N., "Diffusivity and micro-hardness of blended cement materials exposed to external sulfate attack, Cement and Concrete Composites", Volume 34, Issue 1, January 2012, Pages 76-85
32. Igarashi, S., Bentur, A., Mindess, S., "Microhardness Testing of Cementitious Materials", Advanced Cement Based Materials, V.4, pp. 48-57, 1996.

